

EU Wide Monitoring Survey of Polar Persistent Pollutants in European River Waters

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Outline / Contents

List of participants	5
Abstract	9
1. Introduction	10
2. Description of the campaign and selection of sampling sites	11
3. Selection of the target compounds	13
3.1. Perfluorinated compounds (PFCs)	13
3.2. Pharmaceuticals	13
3.3. Pesticides	14
3.4. Benzotriazoles	14
3.5. Endocrine disrupting compounds (EDCs)	14
4. Analytical Methods	15
4.1. Solid-phase extraction (SPE)	15
4.2. Liquid chromatography tandem mass spectrometry (LC-MS ²)	15
4.3. Statistical analyses	18
4.4. Stability of the studied chemicals	19
5. Results and Discussion	20
5.1. SPE-LC-MS ² analysis of the target compounds	20
5.2. Chemical compounds identified	21
5.3. Most pristine rivers	23
5.4. Perfluorinated compounds	24
5.5. Proposed limit or warning levels for surface waters	24
5.6. GIS	24
5.7. River discharge flows and mass flows	24
6. Conclusions and outlook	25
7. Literature references	26
Table Annex: Experimental and analytical data	33

List of abbreviations

APECs	Alkylphenol ethoxycaboxylates
APEOs	Alkylphenol ethoxylate surfactants
APs	Alkylphenols
BPA	Bisphenol A
CRM	Certified reference material
DDT	Dichloro-diphenyl-trichloroethane
EC	European Commission
EDCs	Endocrine disrupting compounds
EDTA	Ethylenediaminetetraacetic acid
EPA	Environmental Protection Agency
EU	European Union
GC	Gas chromatography
GIS	Geographical Information System
HPLC	High performance liquid chromatography
IS	Internal standard
LC	Liquid chromatography
LC-MS ²	Liquid chromatography (tandem) triple quadrupole mass spectrometry
LAS	Linear alkylbenzolsulfonat
LLE	Liquid-liquid extraction
LOD	Limit of detection
MRM	Multiple reaction monitoring
MS	Mass spectrometry
NP	Nonylphenol
NPE ₁ C	Nonylphenol monoethoxy carboxylate (nonylphenoxy acetic acid)
NPEOs	Nonylphenol ethoxylate surfactants
NPE ₁ O	Nonylphenol monoethoxylate
NPE ₂ O	Nonylphenol diethoxylate
NSAID	Non-steroidal anti-inflammatory drug
OP	Octylphenol
QA/QC	Quality assurance / quality control
PE	Polyethylene
PFCs	Perfluorinated compounds
PFOA	Perfluorooctanoate
PFOS	Perfluorooctansulfonate
PNEC	Predicted no-effect concentration
POPs	Persistent organic pollutants
PP	Polypropylene
RP	Reversed-phase
RSD	Relative standard deviation
SDB	Styrol-divinylbenzene
SIM	Selected ion monitoring
SPE	Solid-phase extraction
WFD	Water Framework Directive
WWTP	Wastewater treatment plant

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The following synopsis lists the participants in the exercise, who actively contributed to the project. The names of the persons listed may not be complete as many hands supported the project behind the scene. This important contribution is however gratefully acknowledged, too.

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Abstract

This study provides the first EU-wide reconnaissance of the occurrence of polar organic persistent pollutants in European river waters. 122 individual water samples from over 100 European rivers, streams or similar water bodies from 27 European Countries were analysed for 35 selected compounds, comprising pharmaceuticals (e.g. carbamazepine, diclofenac), antibiotics (sulfamethoxazole), pesticides (e.g. 2,4-D, mecoprop, bentazone, terbutylazine), perfluorinated compounds PFCs (PFOS, PFOA), benzotriazoles (corrosion inhibitors), hormones (estrone, estradiol), and alkylphenolics (bisphenol A, nonylphenol). Only the dissolved (liquid) water phase, and not the suspend material was investigated.

Around 40 laboratories actively participated in this sampling and monitoring exercise organised by the Joint Research Centre's Institute for Environment and Sustainability (JRC-IES) of the European Commission (EC) in autumn 2007. The selection of sampling sites was done by the participating EU Member States.

The most frequently and at the highest concentration levels detected compounds were benzotriazole, caffeine, carbamazepine, tolyltriazole, and nonylphenoxy acetic acid (NPE₁C). Other important substances identified were naproxen, bezafibrate, ibuprofen, gemfibrozil, PFOS, PFOA, sulfamethoxazole, isoproturon, diuron, and nonylphenol. The highest median concentrations of all samples were measured for benzotriazole (226 ng/L), caffeine (72 ng/L), carbamazepine (75 ng/L), tolyltriazole (140 ng/L), and NPE₁C (233 ng/L).

Relatively high perfluorooctanoate (PFOA) levels were detected in the Rivers Danube, Scheldt, Rhone, and Wyre, and “elevated” perfluorooctansulfonate (PFOS) concentrations in the Rivers Scheldt, Seine, Krka, Severn, Rhine, and Llobregat. A higher median concentration for all river samples was found for PFOS (6 ng/L), compared to PFOA (3 ng/L).

Only about 10 % of the river water samples analysed could be classified as “very clean” in terms of chemical pollution, since they contained only a few compounds in very low concentrations. The most pristine water samples came from Estonia, Lithuania, and Sweden.

For the target compounds chosen, we are proposing limit values in surface waters which are not based on eco-toxicological considerations; these warning levels are (for most compounds) close to the 90th percentile of all water samples analysed.

A first EU-wide data set has been created on the occurrence of polar persistent pollutants in river surface waters to be used for continental scale risk assessment and related decision support.

1. Introduction

The increasing worldwide contamination of freshwater systems with thousands of industrial chemical compounds is one of the key environmental problems facing humanity today. More than one-third of the Earth's accessible renewable freshwater is used for agricultural, industrial, and domestic purposes, and most of these activities lead to water contamination with numerous synthetic compounds. Chemical pollution of natural waters has already become a major public concern in almost all parts of the world (Kolpin et al., 2002; Schwarzenbach et al., 2006).

About 300 million tons of synthetic compounds annually used in industrial and consumer products partially find their way into natural waters. Additional pollution comes from diffuse sources from agriculture, where 140 million tons of fertilizers and several million tons of pesticides are applied each year. In the European Union (EU), for instance, there are more than 100,000 registered chemicals, of which 30,000 to 70,000 are in daily use (EINECS, European Inventory of Existing Chemical Substances) (URL1; Richardson, 2007; Schwarzenbach et al., 2006).

Research has shown that many “new”, previously unknown, compounds enter the environment, disperse, and persist to a greater extent than first anticipated. These chemicals have been found ubiquitously in natural waters, not only in industrialized areas but also in more remote environments. Some chemicals are not degraded at all (e.g., heavy metals) or only very slowly (e.g., persistent organic pollutants such as DDT, lindane, EDTA, perfluorinated compounds (PFCs), or even some pharmaceuticals such as carbamazepine or sulfamethoxazole). They can therefore be transported via water or air to locations hundreds or even thousands of miles away from their source (Reemtsma et al., 2006; Schwarzenbach et al., 2006; Yamashita et al., 2008). Polar persistent water soluble chemicals infiltrate into ground and drinking waters.

Those compounds that are less persistent and not prone to long-range transport may still be of concern if they are continuously emitted or form problematic (bio)transformation products. Examples of this category include pharmaceuticals and other personal care products, and degradation products of surfactants such as nonylphenol (Jonkers et al., 2001; Knepper et al., 2003).

Although most of these compounds are present at low concentrations, many of them raise considerable toxicological concerns, particularly when present as components of complex mixtures. It is very difficult to assess the effect on the aquatic environment of the thousands of synthetic and natural trace contaminants that may be present in water at low to very low concentrations (pg/liter to ng/liter) (Schwarzenbach et al., 2006).

To tackle these problems, the European Water Framework Directive (WFD) (EC, 2000) sets up environmental objectives to achieve “good water status” for all European waters by 2015, and establishes a clear framework to enable these objectives to be achieved. An overview of the European dimension of the problem would be beneficial for both, the scientific community, in order to develop new research initiatives on most pressing issues, and the policy making community, as exemplified by the recent developments in the implementation of the WFD with the need to identify “river basin specific pollutants”.

Surprisingly, little is known about the extent of environmental occurrence, transport, and ultimate fate of many synthetic organic chemicals after their use, particularly, personal care products, pharmaceuticals, new pesticides, and industrial chemicals. In a recent European study on persistent polar pollutants (P^3) in waste water treatment plants (WWTPs) and surface waters (Remmetsma et al., 2006), 36 polar compounds, comprising household and industrial chemicals, pharmaceuticals, and personal care products, were analysed in the effluents of eight municipal WWTPs from four countries. The compounds detected at the highest concentration levels were EDTA (median concentration 60 $\mu\text{g/L}$), and sulfophenyl carboxylates, a group of biodegradation intermediates of the anionic LAS surfactants (57 $\mu\text{g/L}$), benzotriazoles (3 $\mu\text{g/L}$), and benzothiazole-2-sulfonate, diclofenac, and carbamazepine with concentrations in the range of 1-10 $\mu\text{g/L}$, followed by some flame retardants, naphthalene disulfonates, and personal care products in the range of 0.1-1 $\mu\text{g/L}$. EDTA, which is not readily biodegradable and very polar, was recognized as the single anthropogenic organic compound detected in European surface waters at highest concentrations. In surface waters downstream Berlin it was regularly detected in the low $\mu\text{g/L}$ range (Quintana and Reemtsma, 2007; Reemtsma et al., 2006).

During the last years, several occurrence studies on different organic chemicals in individual European countries have been performed (Blanchoud et al., 2007; Calamari et al., 2003; Céspedes et al., 2006; Claver et al., 2006; Fatta et al., 2007; Gros et al., 2006; Konstantinou et al., 2006; Kuster et al.; Lekkas et al., 2004; Loos et al., 2007 and 2008a; Noppe et al., 2007a,b; McLachlan et al., 2007; Moldovan, 2006; Peschka et al., 2006; Planas et al., 2006; Quintana et al., 2001; Roberts and Thomas, 2006; Rodriguez-Mozaz et al., 2004b; Stachel et al., 2003; Tamtam et al., 2008; Tixier et al., 2003; Thomas and Hilton, 2004; Wiegel et al., 2004; Vethaak et al., 2005).

The Joint Research Centre's Institute for Environment and Sustainability (JRC-IES) has therefore organised an EU-wide perspective on the occurrence of some selected polar persistent organic pollutants in European river waters to obtain a European overview on this problematic.

2. Description of the campaign and selection of sampling sites

Since the sampling points in this study have been chosen by the individual Member State laboratories, many different water body types make part of this exercise, big and small, contaminated and pristine rivers and streams. Therefore, the results of this study can be considered to be representative of all streams and rivers in Europe. It must be noted that big rivers and small streams are difficult to compare in terms of organic pollution. Small contaminated streams might not have a big relevance for the overall "environmental burden" of an ecosystem. For this reason, the Member States were asked to provide also the individual discharge flow data of the rivers and streams in cubic meters per second (m^3/s). In total, 122 sampling stations from European streams, rivers and similar water bodies were screened in this study. All samples were shipped to the facilities of the JRC' IES-Laboratory for analysis by means of SPE-LC-MS²; 35 chemical compounds were identified and quantified. An EU map with all sampling sites is given in Figure 1.

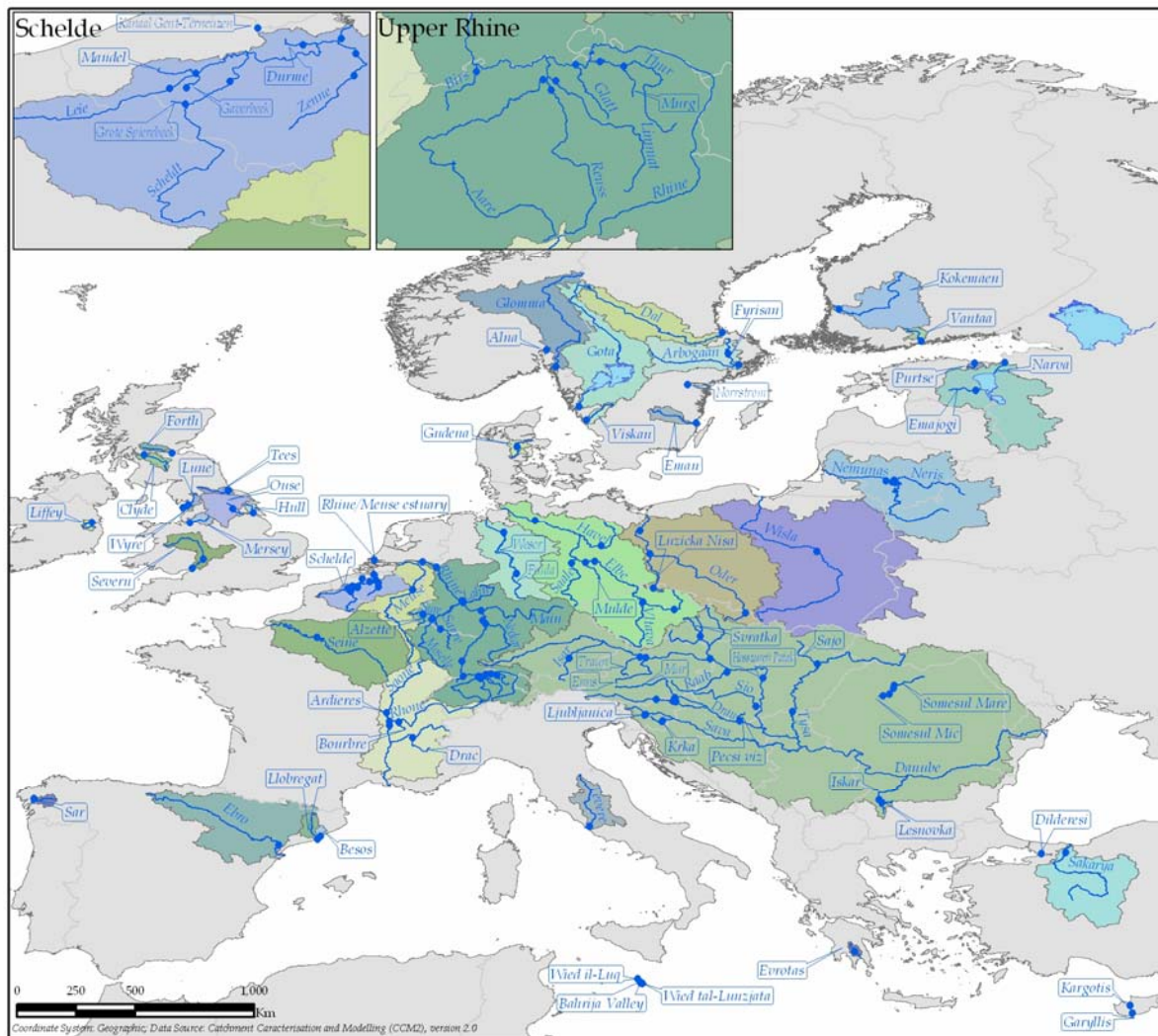


Figure 1: EU map with all sampling sites

Water sampling was performed by the participating Member States laboratories. The JRC gave advice to all laboratories to perform the sampling preferably in the middle of the stream (from a bridge), or, when this was not possible, from the shore. Moreover, samples should have been collected below the water surface (approx. 30 cm). Methanol pre-cleaned PE or PP plastic bottles (0.5 L or 1 L) were provided to all laboratories and sampling teams. The EU Member States were asked to fill these bottles, leaving a small air head-space, and storing them in a fridge at $\sim 4^{\circ}\text{C}$ before dispatch by fast courier to Ispra (Italy). The samples were shipped cooled with freezing elements in styropor boxes, and were extracted at least two weeks after sampling.

From Italy only one sample was included in the study because the Po River basin was investigated in detail before (Loos et al., 2008a).

3. Selection of the target compounds

The target compounds (Table 1) were selected because previous research identified them as prevalent in the environment. Another selection criterion was their relative easy extraction behavior by SPE (at neutral pH) and the strait-forward LC-MS² analysis for those compounds. The pharmaceuticals and pesticides selected are among the most commonly used substances in medicine and agriculture.

3.1. Perfluorinated compounds (PFCs)

These chemicals have unique properties of repelling both water and oil. Together with their chemical and thermal stability, they have found many useful applications, e.g. as surface protectors in carpets, leather, paper, food containers, polishes, and fire-fighting foams. In general, they are used in water repellent surface treatment applications (e.g. Teflon[®], Goretex[®]). The two most important compounds are perfluorooctansulfonate (PFOS), and perfluorooctanoate (PFOA). Contrary to other classical persistent organic pollutants (POPs), these chemicals are primarily emitted to water, they accumulate in surface waters, and water is the major reservoir of PFCs in the environment, as well as the most important medium for their transport. More information on PFCs can be found in the recent literature (Loos et al., 2008a; McLachlan et al., 2007; Yamashita et al., 2005).

3.2. Pharmaceuticals

Pharmaceutically active compounds have been observed repeatedly in surface water and in groundwater worldwide (Calamari et al., 2003; Gros et al., 2006; Heberer, 2002; Petrovic et al., 2005; Tauxe-Wuersch et al., 2005; Tixier et al., 2003; Wiegel et al., 2004). After application, many pharmaceuticals used in human medical care are excreted as the parent substances or water-soluble metabolites. Polar persistent pharmaceutical compounds such as carbamazepine, diclofenac, or clofibric acid are not or only partially eliminated in conventional waste water treatment plants (WWTPs) with biological treatment and subsequently can enter surface waters (Ternes, 1998). The incomplete removal of several pharmaceutical products during aerobic waste water treatment has been reported (for carbamazepine up to 10%; diclofenac is degradable up to 60%; ibuprofen is quite easily degradable) (Joss et al., 2005; Lindqvist et al., 2005; Santos et al., 2007; Ternes, 1998). Some compounds can only be removed with advanced oxidation processes (AOPs) using ozon or hydrogenperoxide (Bernard et al., 2006; Canonica et al., 2008; Gebhardt and Schroeder, 2007; Hu et al., 2007; Nakadaa et al., 2007). Under certain circumstances some pharmaceuticals may even percolate into ground- and drinking water (Scheytt et al., 2005; Ternes et al., 2002; Loos et al., 2007a).

Pharmaceuticals have usually been analysed in effluents of WWTPs, but rarely in surface waters. Wiegel and coworkers reported median carbamazepine levels in the River of 55 ng/L, and in the tributaries Mulde 100 ng/L, and Elster 200 ng/L (Wiegel et al., 2004); diclofenac levels were around 20 ng/L, and ibuprofen ~ 10 ng/L. Heberer (Heberer, 2002) has reported carbamazepine concentrations of up to 1075 ng/L in surface water samples in Berlin (Germany).

Use of diclofenac in animals (cows) has been reported to have led to a sharp decline in the vulture population in the Indian subcontinent, up to 95% in some areas. The

mechanism is probably renal failure, a known side-effect of diclofenac. Vultures eat the carcasses of domesticated animals that have been administered veterinary diclofenac, and are poisoned by the accumulated chemical ([URL2](#)).

3.3. Pesticides

The pesticides chosen for this monitoring study comprised four priority substances of the WFD (atrazine, simazine, diuron, isoproturon), degradation products (e.g. desethyl-atrazine), and some other important pesticides (bentazone, 2,4-D, mecoprop, and terbutylazine) which might become priority compounds in the future or are relevant as river basin specific pollutants in selected European regions ([EU, 2000 and 2001](#)).

An EU “Thematic Strategy on the Sustainable Use of Pesticides” ([EU, 2006](#)) calls for environmental monitoring to be done for other new pesticides in order to verify if the concentrations in the aquatic environment are “safe”.

The selection of the most water relevant compounds from a large list of pesticides in use in Europe remains a challenge to be solved.

3.4. Benzotriazoles

Interest in benzotriazoles is emerging ([Richardson, 2007](#)). Benzotriazoles are complexing agents that are widely used as anticorrosives in industrial and household applications (e.g., in engine coolants, aircraft deicers, or antifreezing liquids, or silver protection in dish washing liquids). Benzotriazoles are weakly basic compounds of high polarity.

The two common forms, benzotriazole and tolyltriazole (methyl-benzotriazole), are soluble in water, resistant to biodegradation, and are only partially removed in wastewater treatment. They are ubiquitous environmental contaminants, but have a limited biological activity; for example, acute toxicity to aquatic organisms is in the low to moderate mg/L range ([Weiss and Reemtsma, 2005](#), [Weiss et al., 2006](#)).

3.5. Endocrine disrupting compounds (EDCs)

It was first reported in 1994 that effluents from UK wastewater treatment plants (WWTPs) were estrogenic to fish. In the following years the endocrine-disrupting phenomenon became an important matter of concern. Endocrine-disrupting compounds (EDCs) are environmental contaminants that disturb normal endocrine function and cause male reproductive dysfunction in humans and wildlife ([Jobling et al., 1998](#); [Wang et al., 2008](#)).

EDCs mainly include natural and synthetic hormones, phytoestrogens, estrogen mimics such as alkylphenols, alkylphenol ethoxylates (APEOs), bisphenol A, metabolites of APEOs (NPE₁C), and others.

Among the wide range of substances with endocrine-disrupting properties, natural and synthetic estrogens (estrone, 17 β -estradiol, estriol, and ethynylestradiol) are of particular interest due to their high estrogenic potency ([Gabet et al., 2007](#); [Wang et al., 2008](#)).

Bisphenol A (BPA) is a building block of polycarbonate plastics used in products such as baby bottles, hikers’ water bottles, food containers, digital media products (CDs, DVDs), and electronic equipment. It acts as an endocrine disrupter, and has been shown

to lead to obesity, depressed growth rates, and prostate cancer in laboratory animals. Concern has been raised in recent years about the toxicity of BPA to aquatic organisms, which has been mainly related to its estrogenic activity. Predicted no-effect concentrations (PNEC) for BPA in water in the range of 0.1–1 µg/L have been proposed. Occurrence of BPA in the aquatic environment has been widely reported (Fromme et al., 2002; Press-Kristensen et al., 2007; Rodriguez-Mozaz et al., 2007; Stachel et al., 2003; Watabe et al., 2004).

4. Analytical Methods

4.1. Solid-phase extraction (SPE)

The water samples were extracted at the JRC by solid-phase extraction (SPE) with Oasis HLB (200 mg) cartridges. Most water samples contained particles (suspended particle material; SPM) which settled to the bottom of the plastic bottles. The water was not filtered, but decanted into a 500 mL glass bottle (Schott-Duran). Thus, only the dissolved (liquid) water phase was investigated. Before extraction, the samples (500 mL) were spiked with the internal standard (50 µL), which contained the labeled substances PFOA $^{13}\text{C}_4$, PFOS $^{13}\text{C}_4$, carbamazepine d10, simazine $^{13}\text{C}_3$, atrazine $^{13}\text{C}_3$, ibuprofen $^{13}\text{C}_3$, and 4-nonylphenol d8. The spiking level in the water samples was 10 ng/L for PFOA $^{13}\text{C}_4$ and PFOS $^{13}\text{C}_4$, and 100 ng/L for the other labeled compounds. The glass bottles were closed, and then the samples were mixed by shaking (Figure 2).

The SPE procedure for the clean-up and concentration of water samples was performed automatically using an AutoTrace[®] SPE workstation (Caliper Life Sciences). 200 mg (6 mL) Oasis[®] HLB columns (Waters, Milford, MA, USA) were used. The cartridges were activated and conditioned with 5 mL methanol and 5 mL water at a flow-rate of 5 mL min⁻¹. The water samples (400 mL) were passed through the wet cartridges at a flow-rate of 5 mL min⁻¹, the columns rinsed with 2 mL water (flow 3 mL min⁻¹), and the cartridges dried for 30 min using nitrogen at 0.6 bars. Elution was performed with 6 mL methanol. Evaporation of the extracts with nitrogen to 500 µL was performed at a temperature of 35°C in a water bath using a TurboVap[®] II Concentration Workstation (Caliper Life Sciences).

4.2. Liquid chromatography tandem mass spectrometry (LC-MS²)

Analyses were performed by reversed-phase liquid chromatography (RP-LC) followed by electrospray ionization (ESI) mass spectrometry (MS) detection using atmospheric-pressure ionization (API) with a triple-quadrupole MS-MS system. Quantitative LC-MS² analysis was performed in three separate LC-MS² runs (methods 1-3) in the multiple reaction monitoring (MRM) mode. Method 1 comprised the compounds in the negative ionization mode, method 2 those in the positive ionization mode, and method 3 alkylphenolic compounds and estrogens which were analysed with a different HPLC mobile phase.



Figure 2: Sampling bottles and water extracts

LC was performed with an Agilent 1100 Series LC systems consisting of a binary pump, vacuum degasser, autosampler and a thermostated column compartment. LC separations

were performed with a Hypersil Gold column (Thermo Electron Corp., 100 x 2.1 mm, 3 μ m particles). Tandem mass spectrometry was performed on a bench-top triple-quadrupole *quattro micro* MS from Waters-Micromass (Manchester, UK) equipped with an electrospray probe and a Z-spray interface.

The eluants used for the separations of the target analytes were water and acetonitrile. The water phase used was acidified with 0.1 % acetic acid (pH 3.5) when analyzing PFCs, pharmaceuticals, and pesticides in the negative and positive ionization modes. The flow-rate was 0.25 mL min⁻¹. The gradient started with 90 % water and proceeded to 90 % acetonitrile over 25 min, conditions hold for 5 min, returned back to the starting conditions over 5 min, and followed by 5 min equilibration. The alkylphenolic compounds comprising NP, OP, BPA, NPE₁C, and the estradiol hormones were analysed with an water-acetonitrile gradient without the addition of acetic acid. In this case the gradient started with 60 % water. The injection volume was 5 μ L; injection was performed by the autosampler.

Instrument control, data acquisition and evaluation (integration and quantification) were done with MassLynx software. Nitrogen is used as the nebulizer gas and argon as the collision gas. Capillary voltage was operated at 3.2 kV, extractor lens at 1.0 V, and RF lens at 0.0 V. The source and desolvation temperatures were set to 120 and 350 °C under chromatographic HPLC conditions. Cone and desolvation gas flows were 50 and 600 L h⁻¹, respectively. The applied analyser parameters for MRM analysis were: LM 1 and HM 1 resolution 11.0, ion energy 1 1.0, entrance -1 (negative mode), 2 (positive mode), exit 1, LM 2 and HM 2 resolution 11.0, ion energy 2 2.0, multiplier 600 V. The MRM inter-channel delay was 0.05 and the inter-scan delay 0.15.

Collision-induced dissociation (CID) was carried out using argon at approx. 3.5×10^{-3} mbar as collision gas at collision energies of 7 - 40 eV. The optimized characteristic MRM precursor \rightarrow product ion pairs monitored for the quantification of the compounds together with the cone voltage and collision energy are given in Table 2.

Identification, quantification, QA/QC and LODs

The first mass transition in Table 2 was used for quantification, and the second only for confirmation purposes. The internal standards ibuprofen ¹³C₃, atrazine ¹³C₃ and simazine ¹³C₃ came from Cambridge Isotope Laboratories (Andover, MA, USA), carbamazepine d10 from CDN ISOTOPEs (Quebec, Canada), PFOS and PFOA ¹³C₄ from Wellington Laboratories (Guelph, Canada), and 4-n-nonylphenol d8 from Dr. Ehrenstrofer (Augsburg, Germany). The recoveries were determined with spike experiments in the concentration range of 10 and 100 ng L⁻¹ using Milli-Q water (replication n = 6); they were in the range of 50 – 90 % (see Table 2 and (Loos et al., 2007a)).

The compounds were identified by retention time match and their specific LC-MS² MRM transitions. Good performance of the developed analytical methods was demonstrated by successful participation in several interlaboratory exercises on non-steroidal anti-inflammatory drugs (NSAIDs) (Farré et al.), PFCs (van Leeuwen et al., 2008) and nonyl- and octylphenol (Loos et al., 2008b). Quantification of the individual compounds was performed with similar internal standards (IS). For instance, the first compounds (pesticides, pharmaceuticals) in Table 2 were all quantified with the internal standard ibuprofen ¹³C₃. All perfluorinated carboxylates were quantified with PFOA ¹³C₄, and PFOS with PFOS ¹³C₄. Sulfamethoxazole, carbamazepine, caffeine, and the

benzotriazoles were quantified with the IS carbamazepine d10. The pesticides and metabolites were quantified with atrazine $^{13}\text{C}_3$ and simazine $^{13}\text{C}_3$. All compounds in the alkylphenolic compounds group (including the estradiol hormones) were quantified with the IS 4-n-nonylphenol d8. The relative response factors of the compounds in relation to the IS were calculated in all cases. Thus, the reported concentrations are corrected with the recoveries of the compounds. A comparative check of internal quantification was always performed with external quantification.

The compound-dependent method detection limits (MDLs or LODs) for the SPE-LC-MS² procedure were calculated from the mean concentrations of the blanks of the real water samples plus 3 times the standard deviation; 400 mL water was extracted and concentrated to 0.5 mL, which results in an enrichment factor of 800.

Uncertainty

Measurement uncertainties of analytical methods can be calculated by the analysis of certified reference materials (CRM), or from the Z-scores derived from interlaboratory studies. CRMs for polar organics in water samples do not exist. The JRC-IES laboratory participated in two interlaboratory studies on non-steroidal anti-inflammatory drugs NSAIDs (Farré et al.), the 3rd international interlaboratory study on PFCs (van Leeuwen et al., 2008), and a dedicated study on nonyl- and octylphenol (Loos et al., 2008b).

Another possibility to calculate the uncertainty is from the single uncertainty sources in the laboratory, if known (standards, glass ware, balance, etc.). Examples how to calculate the uncertainty of a SPE-GC-MS method by this procedure can be found in (Quintana et al., 2001; Planas et al., 2006). These examples show that typical uncertainties for the analysis of water samples by SPE-GC-MS are around 25-50 %.

4.3. Statistical analyses

Frequency of positive detection (freq) in [%], average, median (med), and percentile 90% (Per90), were quantified with excel software (Microsoft).

4.4. Stability of the studied chemicals

The stability of the target compounds was investigated before the campaign with a spiking experiment at 100 ng/L over a time period of three weeks using a real river water sample (River Olona). The spiked river water sample was stored in the laboratory outside the fridge at $\sim 15^{\circ}\text{C}$ (in the dark). This experiment showed that the polar pharmaceuticals (ibuprofen; diclofenac; ketoprofen; bezafibrate; naproxen) are slowly degraded in water (by a factor of around 20 % after 3 weeks). The limited stability of bisphenol A is well known; nonylphenol has a half-life of ~ 1 month in water (Loos et al., 2007b). All other compounds were relatively stable over this time period.

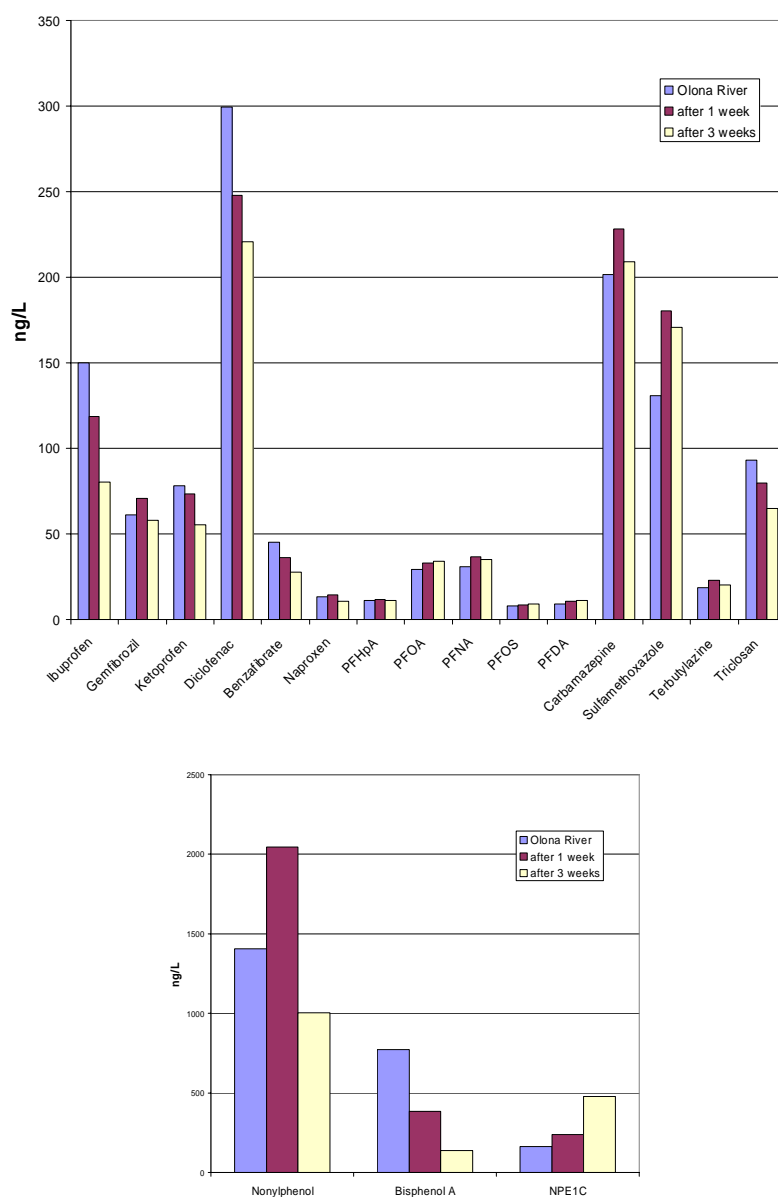


Figure 3: Stability of the target compounds in river water (River Olona)

5. Results and Discussion

5.1. SPE-LC-MS² analysis of the target compounds

The SPE-LC-MS² procedure for the polar organic compounds was developed and optimized before (Loos et al., 2007a, 2008a). Figure 4 shows an exemplary LC-MS² chromatogram of one of the most impacted river water extracts in the negative ionization mode, and Figure 5 in the positive ionization mode.

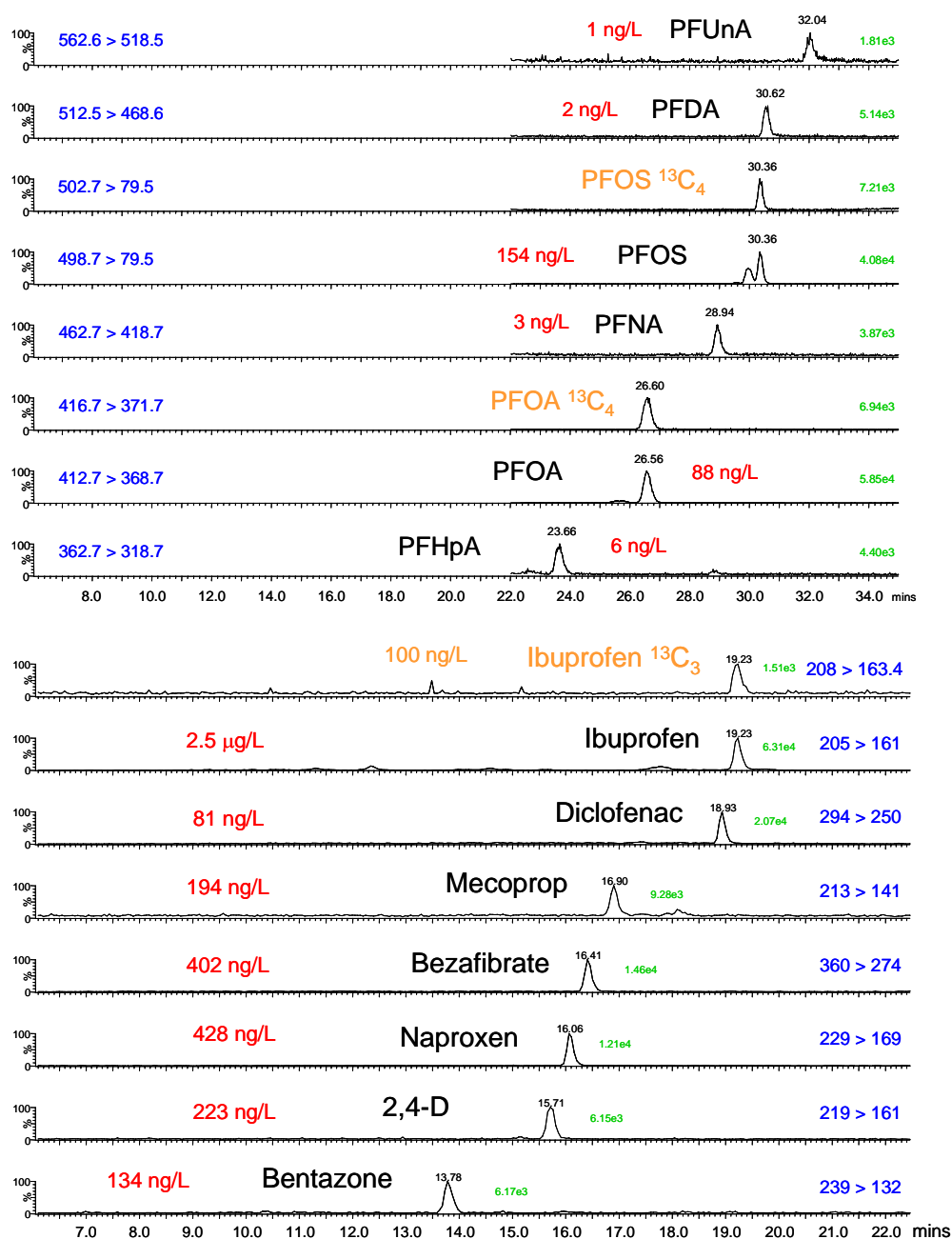


Figure 4: LC-MS² chromatogram of a river water extract, negative mode

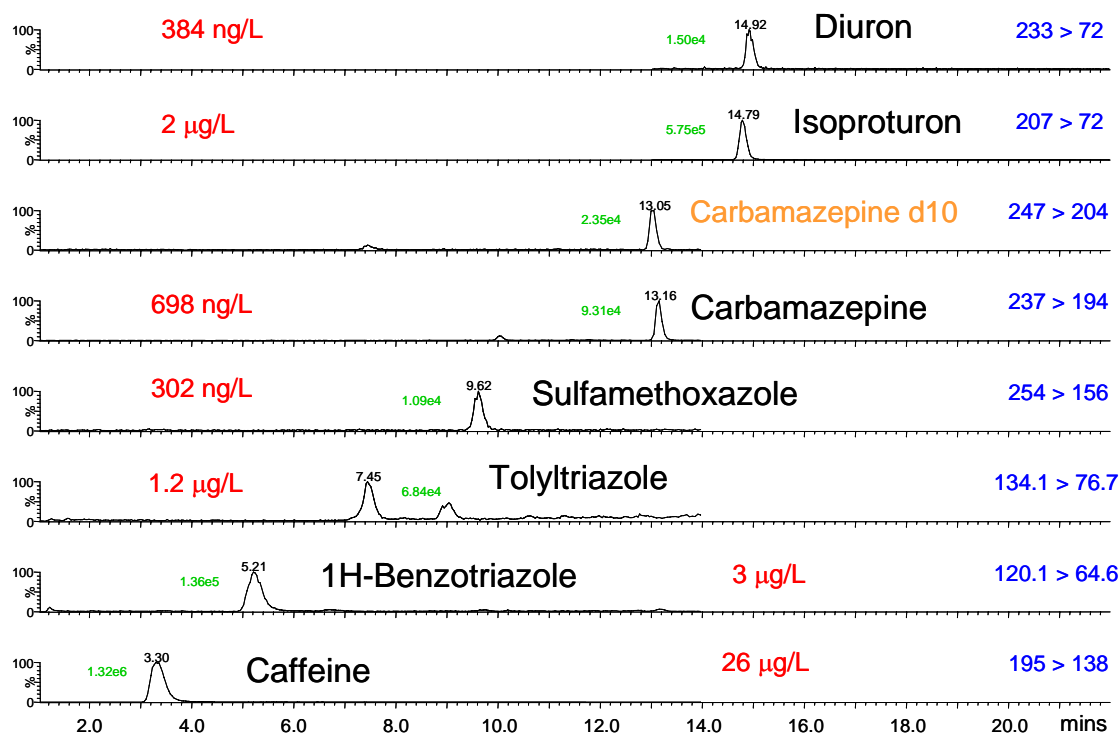


Figure 5: LC-MS² chromatogram of a river water extract, positive mode

5.2. Chemical compounds identified

Table 3 summarizes the analytical results for the polar organic compounds which were measured in the rivers and streams across Europe and all single analytical results are given in Tables 4 and 5. The high overall frequency of detection (above the LOD) is shown by the percentile frequency (freq) of detection for the compounds. The average frequency of detection for all compounds was 61%.

The most frequently detected compounds were 1-nitrophenol (freq 97%), NPE₁C (97%), PFOA (97%), caffeine (95%), carbamazepine (95%), PFOS (94%), benzotriazole (94%), 2,4-dinitrophenol (86%), diclofenac (83%), and tolyltriazole (81%), which were detected in nearly all water samples (Figure 6).

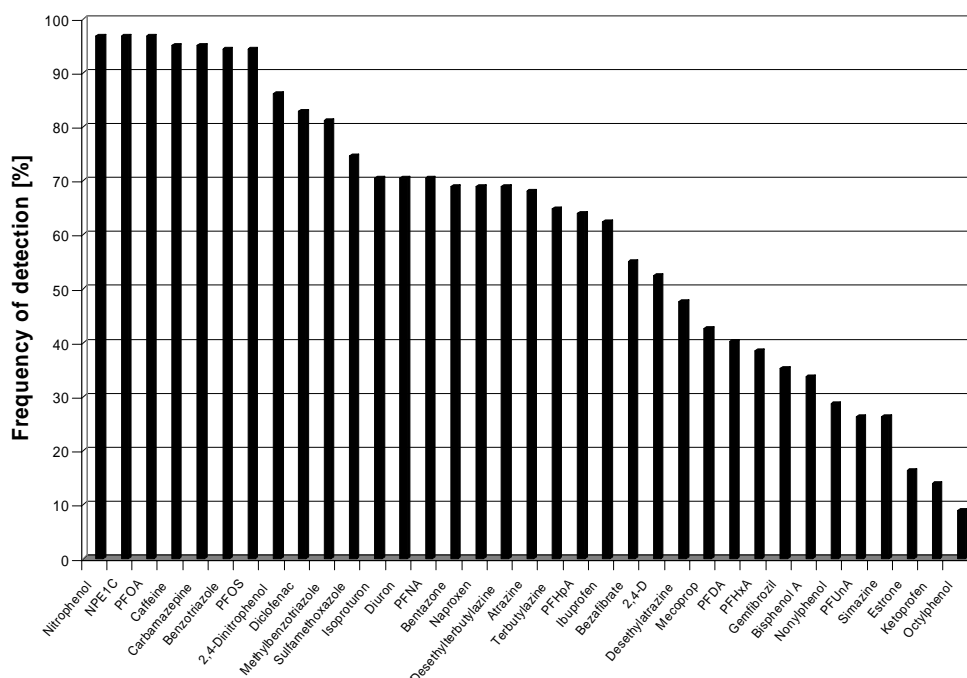


Figure 6: Frequency of detection for the target compounds

The compounds which were detected at the lowest overall frequency were PFUnA (26%), simazine (26%), estrone (16%), ketoprofen (freq 14%), and tert-OP (9%). It must be noted that also 17β -estradiol and 17α -ethinylestradiol were analysed in all samples, but never detected above the detection limit of ~ 5 ng/L (for those compounds).

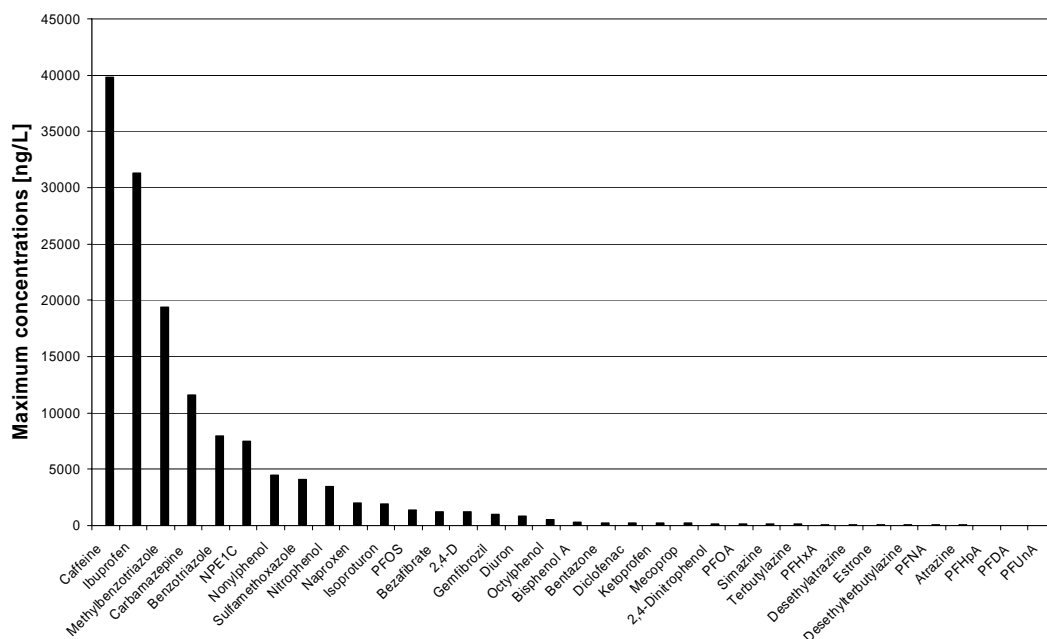


Figure 7: Maximum concentrations of the target compounds

Table 3 shows also the maximum (max) and medium (med) concentration levels for the substances studied. The highest median concentrations were measured for NPE₁C (233 ng/L), benzotriazole (226 ng/L), tolyltriazole (140 ng/L), carbamazepine (75 ng/L), and caffeine (72 ng/L) (Figure 8). In addition, high average concentrations were found as well for ibuprofen (395 ng/L), nonylphenol (134 ng/L), sulfamethoxazole (76 ng/L), isoproturon (52 ng/L), diuron (41 ng/L), PFOS (39 ng/L), naproxen (38 ng/L), bezafibrate (32 ng/L), and gemfibrozil (29 ng/L), showing the relevance of these substances.

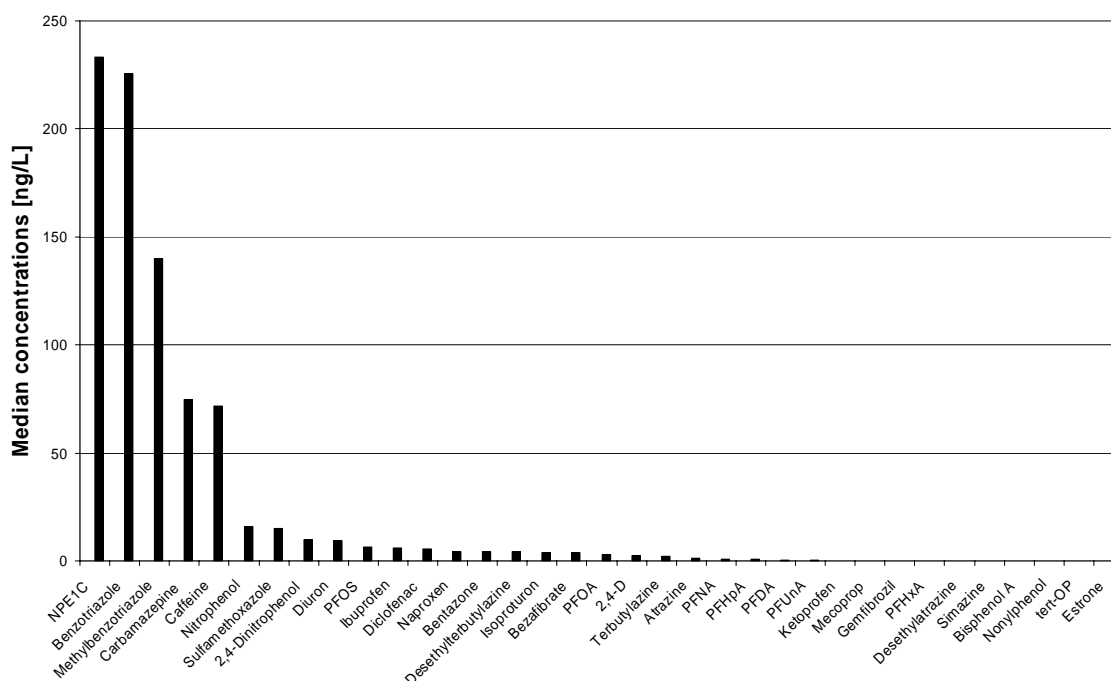


Figure 8: Medium concentrations of the target compounds (122 samples)

The single compounds with the highest maximum concentrations were caffeine (40 µg/L), ibuprofen (31 µg/L), tolyltriazole (20 µg/L), carbamazepine (12 µg/L), and benzotriazole (8 µg/L) (Figure 7).

Pesticides were in general found in relatively low concentration ranges because the survey was conducted in autumn; the single highest pesticide concentration was detected for isoproturon with ~ 2 µg/L.

5.3. Most pristine rivers

Among the 122 river water samples analysed, there were eleven samples which contained only a few chemical substances at very low concentrations. These water samples came from Austria, Denmark, Estonia, Lithuania, Malta, Norway, Slovenia, and Sweden. The compounds detected at low concentrations (< 50 ng/L) in these “clean” water samples were benzotriazole, tolyltriazole, caffeine, and NPE₁C, which shows their ubiquitous occurrence in even remote areas. The most pristine water samples came from Estonia, Lithuania, and Sweden, which might be explained by the low population density in those countries.

5.4. Perfluorinated compounds

In this study special focus was given to the analysis of water-soluble perfluorinated compounds (PFCs) because of their persistent character in water. Perfluorooctanoate (PFOA) has been identified before as a major industrial contaminant present in European rivers ([McLachlan et al., 2007](#); [Loos et al., 2008a](#)). The Po River in N-Italy was identified as the major PFOA source from the European Continent; around 200 ng/L PFOA was found at a median river flow of $\sim 1500 \text{ m}^3/\text{s}$.

In this study we could identify other important European PFOA sources; it was found in the following big rivers: River Danube in Austria (25 ng/L, $\sim 1500 \text{ m}^3/\text{s}$), River Scheldt in Belgium and The Netherlands (88 ng/L and 73 ng/L; $\sim 150 \text{ m}^3/\text{s}$), River Rhone in France (116 ng/L; $\sim 1500 \text{ m}^3/\text{s}$), and the River Wyre in the UK (100 ng/L). These rivers are together with the Po River the major PFOA sources in Europe.

Relatively high PFOS concentrations were found in the Rivers Scheldt in Belgium (154 ng/L) and The Netherlands (110 ng/L), Seine in France (97 ng/L; $\sim 80 \text{ m}^3/\text{s}$), Krka in Slovenia (1371 ng/L; $\sim 50 \text{ m}^3/\text{s}$), Severn in the UK (238 ng/L; $\sim 33 \text{ m}^3/\text{s}$), Rhine in Germany (Wesel; 32 ng/L; $1170 \text{ m}^3/\text{s}$), and in some smaller streams (e.g. in Barcelona, Spain). A higher median concentration for all river samples was found for PFOS (6 ng/L), compared to PFOA (3 ng/L).

However, it must be noted that some big important European Rivers (e.g. Loire (France), Tagus (Spain/Portugal), Shannon (Ireland), and the Volga in East Europe) ([URL3](#); [URL4](#)) were not included in this study.

5.5. Proposed limit or warning levels for surface waters

The objective of this study was not to contribute to the discussion on possible ecotoxicological effects of organic compounds in water. We have calculated for the target compounds the 90th percentile levels (Per90; Table 3) of all 122 water samples analysed. The 90th percentile is the value below which 90 percent of the observations may be found. The limit values proposed for the chemical compounds in surface waters (Table 3; last column) are for most compounds close to these 90th percentile values.

5.6. GIS

The spatial information and attribute data of the sampling points as well as corresponding rivers were converted into KML (Keyhole Markup Language) format using Geographical Information System (GIS) and can be visualised as a map using i.e. Google Earth software ([URL5](#) and [6](#)).

5.7. River discharge flows and mass flows

The participating laboratories were asked to provide river discharge flow data in $[\text{m}^3/\text{s}]$ for the rivers monitored. It is not always easy to obtain these data, but most Member States have provided them. With these data mass flows for the (persistent) chemicals can be estimated. River data bases are available from the European Environment Agency (EEA) ([URL7](#)), and the Water Information System for Europe (WISE) ([URL5](#)).

6. Conclusions and outlook

This was the first EU-wide reconnaissance of the occurrence of polar (persistent) organic pollutants in European river waters. The objective was to collect occurrence data to establish guidance and indications on emerging pollutants in river water. More information on chemical compounds in surface waters is needed, because the increasing chemical pollution of surface and ground waters has largely unknown long-term effects on aquatic life and on human health.

It must be mentioned that only 35 compounds could be analysed in this study. Focus was given to water-soluble polar substances which are well being analysed by LC-MS². However, there are many other organic compounds which are present in surface waters. A list of other possible relevant emerging pollutants can be found on the homepage of the NORMAN project ([URL8](#)), or in selected recent publications cited in the literature references. Interesting compound classes for future EU-wide occurrence studies could be:

- New pesticides and their degradates (EU, 2006; Stackelberg et al., 2004)
- Other pharmaceuticals, antibiotics, or illicit drugs (Carballa et al., 2007; Díaz-Cruz and Barceló, 2005; Gros et al., 2006; Kasprzyk-Hordern et al., 2007; Peschka et al., 2006; Sacher et al., 2001; Stackelberg et al., 2004)
- Personal care products, fragrances (AHTN, HHCB, camphor, musk ketone / xylene), UV filters (sun screen agents), preservatives (parabens), and biocides (Canosa et al., 2006; Kupper et al., 2006; Simonich et al., 2002; Stackelberg et al., 2004)
- Polybrominated biphenyl ethers (PBDEs) and other flame retardants (Guan et al., 2007; Cetin and Obabasi, 2007; Wurl et al., 2006; Streets et al., 2006)
- Benzothiazoles (corrosion inhibitors) (Kloepfer et al., 2004; Ni et al.)

First, reliable analytical methods have to get developed and validated for those new chemicals.

For most of the chemicals analysed no environmental limit values do exist. The WFD introduces environmental quality standards for 41 (groups of) chemicals.

Environmental monitoring campaigns are envisaged for ground water and costal marine waters.

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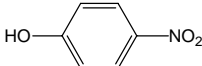
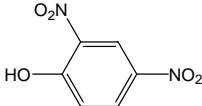
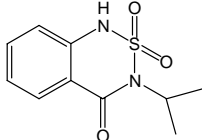
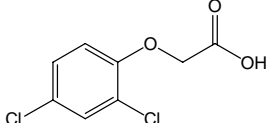
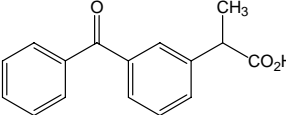
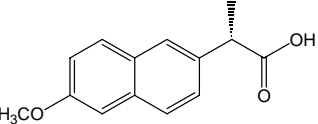
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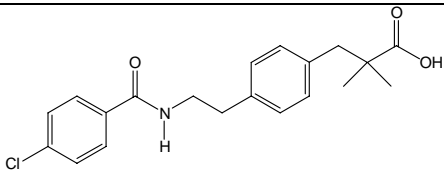
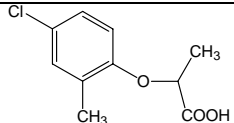
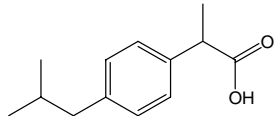
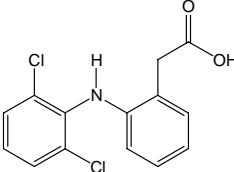
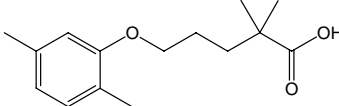
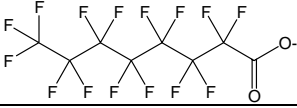
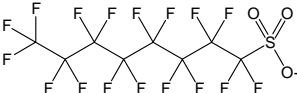
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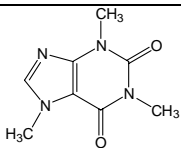
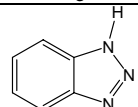
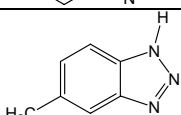
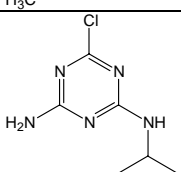
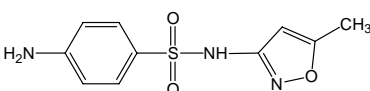
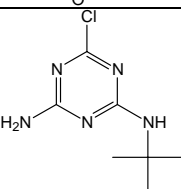
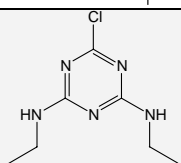
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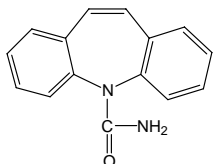
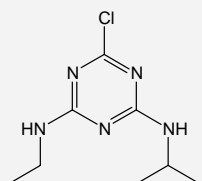
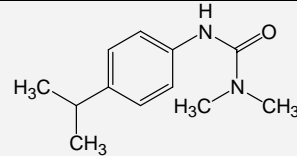
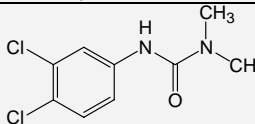
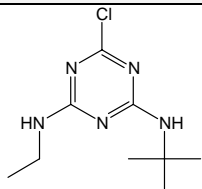
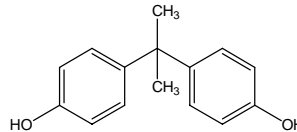
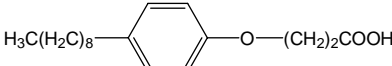
Table Annex: Experimental and analytical data

Table 1: Information to the chemicals studied

Chemical	CAS No.	Structure	Comment	Reference
Negative mode (method 1)				
4-Nitrophenol	100-02-7		Nitrophenols are biorefractory organic compounds which are mainly used in the production of pesticides, explosives, dyes and plasticizers. They enter the environment via wastewater discharges from industry, motor vehicle emissions and contaminant degradations or atmospheric inputs, and thus they are ubiquitous environmental contaminants	
2,4-Dinitrophenol	51-28-5			
Bentazone	25057-89-0		Diazin contact herbicide; low affinity for particulate or organic carbon; log K _{ow} 0.35	URL2
2,4-D (Dichlorophenoxyacetic acid)	94-75-7		One of the most widely used herbicides in the world; aqueous aerobic half-life of ~ 15 days	URL2
Ketoprofen	22071-15-4		NSAID with analgesic and antipyretic effects	Gros et al., 2006 Tixier et al., 2003
Naproxen	22204-53-1		NSAID commonly used for the reduction of moderate to severe pain, fever, and inflammation caused by conditions such as osteoarthritis, rheumatoid arthritis, injury (like fractures), and menstrual cramps	Gros et al., 2006 Joss et al., 2005 Tixier et al., 2003

Bezafibrate	41859-67-0		Fibrate drug used for the treatment of hyperlipidaemia; it helps to lower LDL cholesterol and triglyceride in the blood, and increase HDL	Gros et al., 2006 URL2
Mecoprop	7085-19-0		Hormone-type phenoxy herbicide affecting enzyme activity and plant growth; used on sports turf, for forest site preparation, wheat, barley, and oats, etc.	Blanchoud et al., 2007 URL2
Ibuprofen	15687-27-1		NSAID (analgesic, antipyretic); it is an important non-prescription drug used widely; slowly degraded in aqueous media to hydroxy- and carboxy-ibuprofen	Gros et al., 2006 Joss et al., 2005 Tixier et al., 2003 Winkler et al., 2001
Diclofenac	15307-86-5		NSAID used in human medical care as an analgesic, antiarthritic, antirheumatic compound for reducing pain in conditions such as in arthritis or acute injury	Gros et al., 2006 Joss et al., 2005 Tixier et al., 2003
Gemfibrozil	25812-30-0		Fibrate drug used to lower lipid levels	Gros et al., 2006
Perfluorinated compounds				
PFHxA; perfluorohexanoate	68259-11-0		The most common use of PFOA is as polymerization aid in the production of fluoropolymers such as polytetrafluoroethylene (PTFE), Teflon®, Gore-Tex®; APFO is the ammonium salt of PFOA and the chemical form used in fluoropolymer manufacturing	URL2
PFHpA; perfluoroheptanoate	375-85-9			
PFOA; perfluorooctanoate	335-67-1			
PFNA; perfluorononanoate	375-95-1		Surfactant widely used as stain and water repellent in textiles, paper, leather, waxes, polishes, paints, plates, food-containers, bags, cartoons, hydraulic fluid additive,	URL2
PFOS; perfluorooctansulfonate	EDF-508 Acid: 1763-23-1 NH ₄ ⁺ :			

	29081-56-9		coating additives, or in fire-fighting foams	
PFDA; perfluorodecanoate	335-76-2			
PFUnA; perfluoroundecanoate	2058-94-8			
Positive mode (method 2)				
Caffeine	58-08-2		Xanthine alkaloid compound that acts as a psychoactive stimulant drug	Moldovan, 2006 URL2
1H-Benzotriazole	95-14-7			
1-Methyl-1H-benzotriazole (Tolyltriazole)	13351-73-0		Anticorrosives used e.g. in dish washers	Weiss and Reemtsma, 2005 Weiss et al., 2006
Atrazine-desethyl	6190-65-4		Persistent metabolite of atrazine	Claver et al., 2006 Planas et al., 2006 Rodriguez-Mozaz et al., 2004b
Sulfamethoxazole	723-46-6		Sulfonamide bacteriostatic antibiotic; relatively persistent in water	Gros et al., 2006 Hu et al., 2007 Joss et al., 2005 Tamtam et al., 2008
Terbutylazine-desethyl	30125-63-4		Persistent metabolite of terbutylazine	
Simazine	122-34-9		Triazine herbicide similar to atrazine	Claver et al., 2006 Noppe et al., 2007 Rodriguez-Mozaz et al., 2004b

Carbamazepine	298-46-4		Anti-epileptic and mood stabilizing drug; persistent character ; it has been proposed due to its stability as a possible anthropogenic marker in the aquatic environment	Andreozzi et al., 2003 Clara et al., 2004 Carballa et al., 2007 Heberer, 2002 Gros et al., 2006 Joss et al., 2005
Atrazine	1912-24-9		Triazine herbicide used globally to stop pre- and post-emergence broadleaf and grassy weeds in major crops; it is one of the most widely used herbicides in the USA, but it has been banned in the EU; quite persistent in water and soil; degradation to dealkylated and hydroxyl metabolites	Blanchoud et al., 2007 Claver et al., 2006 Noppe et al., 2007 Rodriguez-Mozaz et al., 2004b
Isoproturon	34123-59-6		Phenylurea herbicide; mobile in soil; in water, it is quite persistent with a half-life of about 30 days	Claver et al., 2006 Blanchoud et al., 2007 Rodriguez-Mozaz et al., 2004b
Diuron	330-54-1		Phenylurea herbicide; its main use is as anti-fouling agent in boat paints; relative persistent in natural waters	Claver et al., 2006 Rodriguez-Mozaz et al., 2004b
Terbutylazine	5915-41-3		Triazine herbicide which replaces atrazine in the EU; less mobile than atrazine	Claver et al., 2006 Noppe et al., 2007
Phenolic compounds (method 3)				
Bisphenol A	80-05-7		Endocrine disrupting compound (EDC) used in plastic materials (see section 3.5)	Fromme et al., 2002 Céspedes et al., 2006 Loos et al., 2007b Rodriguez-Mozaz et al., 2004b
Nonylphenoxyacetic acid NPE ₁ C	3115-49-9		Alkylphenol ethoxycarboxylates (APECs) are recalcitrant metabolites of the APEO surfactants; the most prominent species is nonylphenoxyacetic acid (NPE ₁ C)	Jonkers et al., 2001

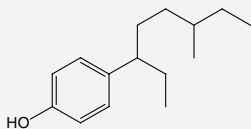
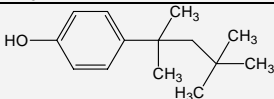
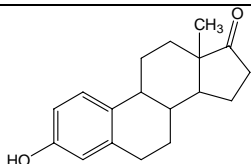
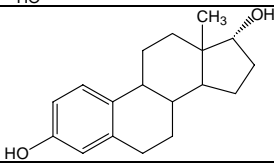
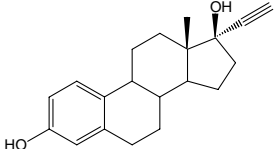
Nonylphenol (NP)	84852-15-3		Alkylphenols are important degradation products of alkylphenol ethoxylates (APEOs) which are nonionic surfactants widely used in agricultural, industrial, and domestic applications; 80 % of the APEO surfactants used are NPEOs, while the remaining 20 % are almost entirely octylphenol isomers (OPEOs)	Céspedes et al., 2006 Loos et al., 2007b
tert-Octylphenol (OP)	140-66-9		Octylphenol has a higher endocrine disrupting potential than NP because it is a single branched isomer	Céspedes et al., 2006 Loos et al., 2007b
Steroid estrogens				
Estrone	53-16-7		Metabolite of estradiol	Gabet et al., 2007 Rodriguez-Mozaz et al., 2004 ^{a,b}
17 β -Estradiol	50-28-2		Natural hormone	Gabet et al., 2007 Rodriguez-Mozaz et al., 2004 ^{a,b}
17 α -Ethinylestradiol	57-63-6		Synthetic hormone used in anti-baby pills	Gabet et al., 2007 Rodriguez-Mozaz et al., 2004 ^a

Table 2: LC-MS² parameters, retention times, recoveries, LODs

Compound	MRM	Cone [V]	Coll.	Ret. Time [min]	Recovery [%]	LOD [ng/L]
Negative mode						
Bentazone	239 > 132	42	27	13.8	62 ± 8	1
2,4-D	219 > 161	20	13	15.7	56 ± 8	1
Ketoprofen	253 > 209	28	10	15.9	71 ± 8	3
Naproxen	229 > 169	26	10	16.1	65 ± 8	1
Bezafibrate	360 > 274	32	17	16.4	66 ± 12	1
Mecoprop	213 > 141	25	14	16.8	62 ± 8	1
Ibuprofen	205 > 161	25	8	19.1	62 ± 12	1
Ibuprofen ¹³ C ₃	208 > 163.4	12	8	19.1	65 ± 9	
Diclofenac	294 > 250	25	13	18.9	65 ± 6	1
Gemfibrozil	249 > 121	27	15	20.6	62 ± 9	1
Perfluorinated compounds						
PFHxA; perfluorohexanoate	312.8 > 268.8	14	10	20.5	61 ± 12	1
PFHpA; perfluoroheptanoate	363 > 319	14	10	23.5	81 ± 14	1
PFOA; perfluorooctanoate	413 > 369	14	10	26.4	85 ± 11	1
PFOA ¹³ C ₄	417 > 372	14	10	26.4	82 ± 9	
PFNA; perfluorononanoate	463 > 419	14	10	28.8	85 ± 9	1
PFOS; perfluorooctansulfonate	499 > 80 (99)	60	47	30.2	65 ± 10	1
PFOS ¹³ C ₄	503 > 80 (99)	60	47	30.2	66 ± 12	
PFDA; perfluorodecanoate	513 > 469	14	11	30.5	76 ± 8	1
PFUnA; perfluoroundecanoate	563 > 519	14	11	32.0	78 ± 13	1
Positive mode						
Caffeine (stimulant)	195 > 138	25	19	3.4	75 ± 8	1
1H-Benzotriazole	120.1 > 64.6 (91.7)	35	20	5.2	56 ± 9	1
1-Methyl-1H-benzotriazole	134.1 > 78.6 (76.7)	40	19	8.9	47 ± 8	1
Atrazine-desethyl	188 > 146	35	16	8.4	71 ± 10	1
Sulfamethoxazole	254 > 156	30	17	9.6	64 ± 9	1
Terbutylazine-desethyl	202 > 146	20	15	11.6	70 ± 8	1
Simazine	202 > 132	40	18	11.6	70 ± 11	1
Simazine ¹³ C ₃	205 > 134	26	18	11.6	72 ± 9	
Carbamazepine	237 > 194	35	18	13.1	68 ± 11	1
Carbamazepine d10	247 > 204	32	20	13.1	69 ± 8	
Atrazine	216 > 174 (132)	35	17	13.9	72 ± 13	1
Atrazine ¹³ C ₃	219 > 177	25	18	13.9	73 ± 8	
Isoproturon	207 > 72	30	17	14.7	72 ± 13	1
Diuron	233 > 72	30	17	14.8	72 ± 12	1
Terbutylazine	230 > 174 (132)	35	17	16.6	69 ± 8	1
Phenolic compounds						
Bisphenol A	227 > 212 (133)	45	30	8.5	89 ± 3	5
Nonylphenoxyacetic acid NPE ₁ C	277 > 219 (133)	35	18	15.4	68 ± 12	2
Nonylphenol	219 > 133 (147)	45	32	20.6	72 ± 5	50*
4n-Nonylphenol d8	227 > 112	45	23		65 ± 5	
tert-Octylphenol	205 > 106	45	20	21.2	52 ± 5	10
Steroid estrogens						
Estradiol	271 > 145 (183)	50	45	8.8	72 ± 12	5
Estrone	269 > 145 (143)	50	45	10.6	54 ± 13	2
17α-Ethinylestradiol	295 > 145 (159)	50	40	10.2	63 ± 1	5

MRM = multiple reaction monitoring; IS = internal standard; coll. = collision energy; SPE recovery rates from 400 mL water spiked at 10 ng/L using 200 mg Oasis HLB cartridges; LOD = method detection limits; n.a. = not applicable; * blank value determined LOD; priority substances of the WFD in blue.

Table 3: Summary of analytical results for polar pollutants in EU Rivers

Chemical	RL [ng/L]	freq [%]	max [ng/L]	Average [ng/L]	med [ng/L]	Per90 [ng/L]	Proposed limit [ng/L]
Negative mode (method 1)							
4-Nitrophenol	1	97	3471	99	16	95	100
2,4-Dinitrophenol	1	86	174	18	10	40	100
Bentazone	1	69	250	14	4	31	100
2,4-D (Dichlorophenoxyacetic acid)	1	52	1221	22	3	35	100
Ketoprofen	3	14	239	10	0	17	100
Naproxen	1	69	2027	38	4	47	100
Bezafibrate	1	55	1235	32	4	56	50
Mecoprop	1	43	194	15	0	54	100
Ibuprofen	1	62	31323	395	6	220	200
Diclofenac	1	83	247	17	5	43	100
Gemfibrozil	1	35	970	29	0	17	50
Perfluorinated compounds							
PFHxA; perfluorohexanoate	1	39	109	4	0	12	30
PFHpA; perfluoroheptanoate	1	64	27	1	1	3	30
PFOA; perfluorooctanoate	1	97	174	12	3	26	30
PFNA; perfluorononanoate	1	70	57	2	1	3	30
PFOS; perfluorooctansulfonate	1	94	1371	39	6	73	30
PFDA; perfluorodecanoate	1	40	7	1	0	1	30
PFUnA; perfluoroundecanoate	1	26	3	0	0	1	30
Positive mode (method 2)							
Caffeine	1	95	39813	963	72	542	1000
1H-Benzotriazole	1	94	7997	493	226	1225	1000
1-Methyl-1H-benzotriazole (tolyltr.)	1	81	19396	617	140	1209	1000
Atrazine-desethyl	1	48	80	7	0	21	100
Sulfamethoxazole	1	75	4072	76	15	104	100
Terbutylazine-desethyl	1	69	76	10	4	24	100
Simazine	1	26	169	10	0	34	1000
Carbamazepine	1	95	11561	248	75	308	100
Atrazine	1	68	46	3	1	6	600
Isoproturon	1	70	1959	52	4	86	300
Diuron	1	70	864	41	10	115	200
Terbutylazine	1	65	124	9	2	29	100
Phenolic compounds (method 3)							
Bisphenol A	5	34	323	25	0	64	100
Nonylphenoxyacetic acid NPE ₁ C	2	97	7491	553	233	987	1000
Nonylphenol	50	29	4489	134	0	268	300
tert-Octylphenol	10	9	557	13	0	0	100
Steroid estrogens							
Estrone	2	16	81	4	0	10	20
17 β -Estradiol	5	0	n.a.	n.a.	n.a.	n.a.	n.a.
17 α -Ethinylestradiol	5	0	n.a.	n.a.	n.a.	n.a.	n.a.

Number of samples, 122; RL (=LOD), reporting limit; freq, frequency of detection [%]; max, maximum concentration; med, median concentration; Per90, 90th percentile [%]; Proposed limit, proposed concentration limit value for surface waters; n.a., not applicable; priority compounds of the WFD in blue.

Table 4: European river water samples analysed

No.	Country	River	Location	Flow [m ³ /s]	Observation	Code
1	Au	Mur	Spielfeld	150		AA00751
2	Au	Danube	Hainburg	2000		AA00759
3	Au	Drau	Lavamund	200		AA00753
4	Au	Enns	Steyr-Pyburg	200		AA00757
5	Au	Traun	Ebelsberg	150		AA00755
6	Be	Zenne	Drogenbos		yellow, particles	AA00763
7	Be	Scheldt	Hemiksem			AA00765
8	Be	Mandel	Wielsbeke		yellow	AA00775
9	Be	Gaverbeek	Deerlijk		foam, yellow, part.	AA00773
10	Be	Leie	Wevelgem			AA00771
11	Be	Kanaal Gent-Terneuzen	Zelzate			AA00761
12	Be	Scheldt	Oudenaarde			AA00767
13	Be	Grote Spierebeek	Dottignies		foam, yellow, part.	AA00769
14	Bu	Iskar	Novi Iskar	12.5		AA00651
15	Bu	Lesnovka	Dolni Bogrov	0.45		AA00647
16	Cyprus	Kargotis	Lefkosia	0.08		AA00894
17	Cyprus	Garryllis	Lemesos	0.005	brown, foam	AA00896
18	Ce	Elbe	Valy	25		AA00607
19	Ce	Vltava	Zelcin	92.2		AA00605
20	Ce	Svratka	Zidlochovice	7.6		AA00603
21	Ce	Lusatian Neisse / Nisa	Hradek nad Nisou	2.7		AA00601
22	Ce	Odra	Bohumin	27.4		AA00599
23	DK	Gudenaa	Tvilum Bro	13.7		AA00618
24	Est	Emajogi	Kavastu	70	yellow	AA00739
25	Est	Purtse	Tallinn			AA00746
26	Est	Narva	Narva	400		AA00750
27	Fi	Vantaa	Helsinki	16.5		AA00620
28	Fi	Kokemäen	Pori	235		AA00622
29	Fr	Drac	Vercors bridge in Grenoble	90.4		AA00849
30	Fr	Saone	Ile Barbe (upstream Lyon)			AA00853
31	Fr	Bourbre	Pont de Cheruy, Chavanoz			AA00857
32	Fr	Ardieres	St Jean, Moulin de Thuaille		yellow	AA00859
33	Fr	Seine	Conflans Saint Honorine	264		AA00851
34	Fr	Rhone	Solaize	1524		AA00855
35	Ge	Rhine	Wesel	1170		AA00793
36	Ge	Isar	München	33.6		AA00805
37	Ge	Saar	Lisdorf	18.0		AA00785
38	Ge	Lahn	Lahnstein	75.4		AA00787
39	Ge	Neckar	Mannheim	239	sediments, dirty	AA00791
40	Ge	Rhine	Koblenz/Rhein	1820		AA00795
41	Ge	Rhine	Burkheim	655		AA00799

42	Ge	Saale	Bernburg	205		AA00803
43	Ge	Elbe	Geesthacht	614		AA00813
44	Ge	Oder	Eisenhüttenstadt	238		AA00817
45	Ge	Main	Kostheim	166	sediments, dirty	AA00789
46	Ge	Rhine	Worms	1380		AA00797
47	Ge	Weser	Langwedel	307		AA00801
48	Ge	Mulde	Dessau	287		AA00807
49	Ge	Elbe	Wittenberg	243		AA00811
50	Ge	Mosel	Koblenz/Mosel	224		AA00821
51	Ge	Havel	Ketzin	45.5		AA00809
52	Ge	Oder	Schwedt	477		AA00815
53	Ge	Fulda	Hann. Münden	92.1		AA00819
54	Greece	Evrotas	Sparta			Evr1
55	Hun	Sio	Szekszard	13		AA00829
56	Hun	Sajo	Kesznyeten	17.5		AA00825
57	Hun	Raba	Gyor	83	yellow	AA00831
58	Hun	Pecsi viz	Kemes	1.7		AA00833
59	Hun	Tisza	Tiszasziget	830		AA00823
60	Hun	Hosszureti Patak	Kamaraerdo	0.21	yellow	AA00827
61	Ir	Liffey	Lucan Bridge	7.9	yellow, dirty	AA00627
62	It	Tevere	Rome	233		EU61
63	Lit	Nemunas	Kaunas	192-220		AA00723
64	Lit	Nemunas	Kaunas, downstream	316-468		AA00727
65	Lit	Neris	Kaunas, upstream	173-184		AA00731
66	Lit	Neris	Kaunas, downstream	173-184		AA00735
67	Lux	Alzette	Ettelbruck			AA01054
68	Lux	Moselle	Grevenmacher			AA01056
69	Lux	Sûre	Amont Erpendange			AA01058
70	Malta		Bahrija Valley			AA00869
71	Malta		Wied il-Luq			AA00873
72	Malta		Wied tal-Lunzjata		insects	AA00871
73	NL	Meuse	Eijsden at border NL-Belgium	211		AA00777
74	NL	Rhine	Lobith	2200		AA00779
75	NL	Rhine/Meuse estuary	Maassluis			AA00781
76	NL	Scheldt	Schaar, estuary at border NL	110		AA00783
77	No	Glomma	Sarpsfoss			AA00654
78	No	Alna	Oslo			AA00624
79	Po	Vistula				AA00888
80	Po	Vistula				AA00890
81	Po	Vistula				AA00892
82	Ro	Somez Mic	before Cluj	15		EU39
83	Ro	Somez Mic	after Cluj	20		EU40
84	Ro	Somez Mic	after Gherla	20		EU41
85	Ro	Somez Mare	before Dej	35		EU42
86	Slovenia	Krka	Before Mun. Novo Mesto	51		AA00632
87	Slovenia	Krka	After Mun Novo Mesto	51		AA00630
88	Slovenia	Krka	Otocec Ob Krki\	51		AA00611

89	Slovenia	Sava	Kresnice			AA00609
90	Slovenia	Ljubljana	Ljubljana			AA00634
91	Slovenia	Ljubljana	Ljubljana		yellow	AA00636
92	Slovenia	Drava	Maribor 1		particles	AA00638
93	Slovenia	Drava	Maribor 2			AA00648
94	Spain	Ebro	Mora la Nova	166.8		AA00876
95	Spain	Llobregat	Barcelona	17		AA00884
96	Spain	Besos	Barcelona	5		AA00886
97	Spain	Sar	Bertamirans	2.5		AA00878
98	Sweden	Dalalven	Alvkarleby	340		AA00670
99	Sweden	Motala	Norrkoping	3.4		AA00674
100	Sweden	Norrstrom	Stockholm	157		AA00686
101	Sweden	Fyrisan	Flottsund	12.8		AA00662
102	Sweden	Eman	Emsforo	28	dirty, partic., yellow	AA00666
103	Sweden	Viskan	Asbro	35		AA00678
104	Sweden	Gota Alv	Alelyckan	556	yellow	AA00682
105	Swiss	Murg	Frauenfeld	1		AA00835
106	Swiss	Glatt	Rheinsfelden	3		AA00839
107	Swiss	Birs	Munchenstein	4		AA00841
108	Swiss	Thur	Andelfingen	10		AA00837
109	Swiss	Aare	Brugg	140		AA00843
110	Swiss	Reuss	Mellingen	45		AA00845
111	Swiss	Limmat	Baden			AA00847
112	UK	Wyre	Fleetwood			AA00710
113	UK	Lune	Lancaster			AA00714
114	UK	Clyde	Glasgow			AA00694
115	UK	Humber	Hull			AA00702
116	UK	Tees	Middlesbrough			AA00698
117	UK	Mersey	Runcorn			AA00705
118	UK	Forth	Edinburgh	47		AA00690
119	UK	Severn	Haw Bridge, Stafford	33.4		AA00718
120	UK	Ouse	Naburn Lock	10.4	yellow	AA00722
121	Tu	Sakarya	Apazari	10		AA00614
122	Tu	Dilderesi	Kocaeli	0.2	dirty, particles	AA00615

Table 5: Analytical results for the river water samples in [ng/L]. “Higher” concentrations are in red; clean, unpolluted water samples are with yellow background; “Zero” means below LOD.

No.	Country	River	Nitrophenol	2,4-Dinitrophenol	Naproxen	Bentazone	2,4-D	Ketoprofen	Mecoprop	Bezafibrate	Ibuprofen	Diclofenac	Gemfibrozil	PFHxA	PFHpA	PFOA	PFNA	PFOS	PFDA	PFUnA
1	Au	Mur	8	0	4	0	0	0	0	26	0	14	0	0	1	3	1	6	1	1
2	Au	Danube	8	11	5	4	4	0	13	15	4	3	0	1	1	25	1	6	0	0
3	Au	Drau	12	7	3	0	0	0	0	5	4	1	0	0	0	1	0	1	0	0
4	Au	Enns	16	0	0	0	0	0	0	0	0	1	0	0	0	1	0	1	0	0
5	Au	Traun	30	12	4	20	0	0	0	7	63	5	0	0	1	2	0	3	0	0
6	Be	Zenne	147	45	92	26	0	149	54	68	835	47	9	5	2	18	2	49	2	1
7	Be	Scheldt	16	3	0	71	8	0	32	0	0	2	0	21	6	88	3	154	2	1
8	Be	Mandel	361	92	151	0	84	0	73	86	1105	41	0	35	6	48	3	97	1	1
9	Be	Gaverbeek	2055	0	428	134	233	223	194	402	2518	81	0	11	4	11	0	32	0	0
10	Be	Leie	61	29	74	0	0	45	73	215	351	21	17	8	6	12	7	76	3	1
11	Be	Kanaal Gent-Tern.	20	61	10	250	101	0	120	78	8	15	14	11	6	26	13	76	5	2
12	Be	Scheldt	31	40	0	43	35	0	174	92	159	23	11	0	0	10	4	41	2	1
13	Be	Grote Spierebeek	880	0	79	0	37	0	71	0	376	30	0	0	0	174	57	0	6	0
14	Bu	Iskar	54	8	4	10	15	0	0	0	222	44	2	0	0	2	1	3	0	0
15	Bu	Lesnovka	37	6	0	28	21	0	0	0	0	3	0	0	0	1	0	1	0	0
16	Cyprus	Kargotis	5	5	0	0	0	0	0	0	0	2	0	0	0	0	0	1	0	0
17	Cyprus	Garyllis	336	131	9	65	0	0	75	1235	518	175	970	47	17	79	3	56	1	0
18	Ce	Elbe	0	35	5	4	0	0	0	5	92	7	0	12	1	7	2	19	1	0
19	Ce	Vltava	7	7	11	12	3	0	0	4	85	11	0	0	1	3	1	5	0	0
20	Ce	Svratka	6	20	7	7	7	0	0	0	28	18	0	0	1	5	1	4	1	0
21	Ce	Lusatian Neisse	45	71	17	0	0	53	0	9	389	16	0	0	0	4	10	81	1	1
22	Ce	Odra	59	46	6	10	5	0	10	3	173	11	0	0	0	0	1	6	0	0
23	DK	Gudenaa	3	9	0	3	0	0	0	0	0	0	0	0	0	2	1	1	0	0
24	Est	Emajogi	14	14	0	2	0	0	0	0	6	3	0	0	0	1	0	1	0	0
25	Est	Purtse	6	0	0	0	0	0	0	0	0	1	0	0	0	1	0	0	0	0
26	Est	Narva	9	7	0	1	0	0	0	0	3	2	0	0	0	0	1	1	0	0
27	Fi	Vantaa	11	174	0	0	0	0	0	0	0	0	0	22	2	7	16	53	1	3
28	Fi	Kokemäen	9	11	4	0	0	0	0	0	8	0	0	0	1	2	1	3	0	0
29	Fr	Drac	194	10	2	0	15	0	0	6	17	0	0	9	3	15	4	8	7	2
30	Fr	Saone	23	17	4	15	26	0	0	9	23	1	4	3	1	6	2	30	1	0
31	Fr	Bourbre	49	17	18	3	9	0	0	27	45	9	18	3	2	12	11	37	2	1
32	Fr	Ardieres	42	15	3	0	2	0	0	0	9	2	2	0	1	1	1	5	0	0
33	Fr	Seine	33	14	47	7	10	67	14	348	66	17	34	4	2	16	1	97	1	0
34	Fr	Rhone	30	12	7	4	6	14	0	15	46	2	6	19	1	116	2	22	0	1
35	Ge	Rhine	15	14	10	20	4	0	26	54	14	16	2	6	1	11	1	32	1	0
36	Ge	Isar	14	4	0	0	0	0	0	2	0	1	0	0	1	4	2	2	1	0
37	Ge	Saar	0	15	16	4	5	0	11	76	51	35	5	0	1	5	1	12	1	0
38	Ge	Lahn	6	7	5	9	0	0	4	23	31	7	1	0	0	2	0	6	0	0
39	Ge	Neckar	3	24	4	7	0	0	35	32	18	13	6	0	1	4	1	18	1	0

No.	Country	River	Benzo- triazole	Caffeine	Desethyl- Atrazine	Carbamazepine	Sulfamethox azole	Simazine	Desethylter- butylazine	Methylbenzo triazole	Atrazine	Isoproturon	Diuron	Terbutyl- azine	NPE1C	Nonylphenol	Bisphenol A	Estrone	tert-OP
1	Au	Mur	129	73	0	36	0	0	0	65	1	6	1	1	413	0	97	0	0
2	Au	Danube	226	91	10	50	9	0	8	121	2	7	0	2	403	0	0	0	0
3	Au	Drau	34	29	0	12	0	0	0	0	1	1	4	0	39	0	246	0	0
4	Au	Enns	29	43	0	6	0	0	0	21	1	0	0	0	177	0	0	0	0
5	Au	Traun	369	33	39	59	8	0	24	240	6	77	3	5	200	535	0	0	0
6	Be	Zenne	1390	1454	30	1005	153	52	8	1409	7	196	116	12	6339	1173	0	15	50
7	Be	Scheldt	339	11	14	202	32	76	44	568	8	42	207	52	228	48	0	0	0
8	Be	Mandel	2195	11883	0	652	250	115	52	8371	5	195	210	124	4356	390	0	78	58
9	Be	Gaverbeek	3029	26353	0	698	302	169	28	1151	3	1959	384	36	7491	3492	0	81	168
10	Be	Leie	1225	365	33	348	136	0	7	2284	6	40	111	6	1239	782	172	11	28
11	Be	Kanaal Gent-Tern.	506	27	21	309	52	69	69	2459	9	32	341	76	488	82	10	0	0
12	Be	Scheldt	724	39	25	522	73	35	11	1045	8	276	239	18	1502	4489	57	0	75
13	Be	Grote Spierebeek	1034	3757	0	842	91	95	24	1214	3	767	156	30	6906	0	0	0	0
14	Bu	Iskar	329	2152	43	205	300	0	0	161	2	0	0	0	1727	220	223	55	0
15	Bu	Lesnovka	0	467	0	12	20	0	0	0	1	0	0	0	410	270	0	19	0
16	Cyprus	Kargotis	6	99	0	4	0	0	0	0	0	0	1	0	133	0	0	0	0
17	Cyprus	Garyllis	2743	487	0	11561	4072	0	0	3041	0	0	20	0	2132	50	0	3	0
18	Ce	Elbe	128	176	7	76	54	0	17	123	2	15	10	8	903	0	0	0	0
19	Ce	Vltava	174	42	11	113	61	0	27	199	3	11	46	25	478	0	0	0	0
20	Ce	Svratka	217	48	11	214	87	0	54	174	3	6	50	60	767	0	23	0	0
21	Ce	Lusatian Neisse/Nisa	417	549	9	127	100	0	5	1021	2	2	16	4	716	230	323	11	0
22	Ce	Odra	290	285	5	186	36	0	6	228	3	21	16	5	290	0	53	0	0
23	DK	Gudenaa	33	12	0	15	0	0	4	64	1	0	8	3	632	0	0	0	0
24	Est	Emajogi	13	22	0	15	0	0	0	0	0	0	2	0	74	0	0	0	0
25	Est	Purtse	0	22	0	0	0	0	0	90	0	0	0	0	16	0	0	0	0
26	Est	Narva	0	15	0	3	0	0	1	0	0	0	2	0	30	0	0	0	0
27	Fi	Vantaa	30	74	0	11	0	0	0	60	0	0	73	0	438	0	0	0	0
28	Fi	Kokemäen	103	57	0	54	9	0	0	1934	1	2	2	0	523	0	0	0	0
29	Fr	Drac	23	129	0	7	0	0	0	78	0	269	52	2	33	0	0	0	0
30	Fr	Saone	140	78	14	49	9	16	8	108	2	24	40	7	208	0	0	0	0
31	Fr	Bourbre	532	310	38	83	11	15	2	330	5	2	11	0	361	243	0	3	0
32	Fr	Ardieres	57	70	8	35	0	16	17	55	0	1	37	5	147	88	0	0	0
33	Fr	Seine	966	172	44	204	159	0	8	622	3	4	39	3	964	0	0	10	0
34	Fr	Rhone	266	262	13	49	9	0	8	250	2	7	14	7	523	120	64	0	21
35	Ge	Rhine	1222	190	8	203	82	0	9	701	2	40	20	7	189	100	34	0	0
36	Ge	Isar	82	74	0	14	0	0	1	11	0	0	2	0	245	0	0	0	0
37	Ge	Saar	1260	395	9	456	104	0	2	2558	2	52	13	0	279	0	0	0	0
38	Ge	Lahn	504	142	0	73	30	0	5	92	0	187	7	6	153	0	0	0	0
39	Ge	Neckar	711	138	4	133	44	0	4	394	1	453	9	3	238	0	0	0	0

No.	Country	River	Nitrophenol	2,4-Dinitrophenol	Naproxen	Bentazone	2,4-D	Ketoprofen	Mecoprop	Bezafibrate	Ibuprofen	Diclofenac	Gemfibrozil	PFHxA	PFHpA	PFOA	PFNA	PFOS	PFDA	PFUnA
40	Ge	Rhine	14	15	5	17	0	0	19	29	16	11	6	2	1	3	1	17	1	0
41	Ge	Rhine	13	12	4	1	3	0	21	5	5	5	0	1	1	3	1	21	0	0
42	Ge	Saale	11	5	3	13	19	0	7	30	26	13	1	1	1	4	2	9	1	0
43	Ge	Elbe	5	6	0	17	0	0	5	29	3	7	0	2	1	5	1	11	0	0
44	Ge	Oder	0	13	4	6	13	0	0	0	9	4	0	0	0	2	1	5	0	0
45	Ge	Main	18	12	11	20	6	0	8	48	8	23	3	0	1	4	1	17	1	1
46	Ge	Rhine	16	16	5	52	3	6	32	12	5	7	14	2	1	3	1	15	0	0
47	Ge	Weser	13	10	3	11	0	0	6	12	0	10	2	11	1	5	0	8	0	0
48	Ge	Mulde	16	16	4	10	6	0	5	27	19	13	4	6	2	8	1	13	1	0
49	Ge	Elbe	44	12	4	3	3	0	7	11	21	8	0	1	1	6	1	19	0	0
50	Ge	Mosel	22	25	13	11	7	0	19	29	15	12	3	1	1	3	1	18	0	0
51	Ge	Havel	7	15	2	2	0	25	9	21	4	7	0	0	1	8	1	9	1	0
52	Ge	Oder	6	7	5	3	26	0	2	0	11	4	0	0	0	2	1	4	0	0
53	Ge	Fulda	4	14	12	9	0	0	10	19	7	17	4	23	3	8	1	4	0	0
54	Greece	Evrotas	52	7	0	0	3	29	0	0	0	6	0	0	1	1	1	0	0	1
55	Hun	Sio	61	72	8	49	11	0	0	7	0	16	65	0	1	5	1	41	0	0
56	Hun	Sajo	87	40	21	83	0	0	0	4	60	17	9	0	0	2	1	5	0	0
57	Hun	Raba	7	80	4	24	0	0	0	11	0	7	0	0	0	3	1	9	1	1
58	Hun	Pecsi viz	40	82	8	9	16	0	0	11	0	48	36	0	1	4	1	6	0	0
59	Hun	Tisza	8	23	0	8	7	0	0	0	11	3	0	0	0	1	0	3	0	0
60	Hun	Hosszureti Patak	80	0	15	0	14	0	0	27	0	247	48	0	2	32	2	33	1	0
61	Ir	Liffey	9	9	17	0	8	0	0	0	85	9	9	0	1	3	1	3	1	1
62	It	Tevere	37	10	155	0	3	161	6	35	88	9	70	0	3	13	1	7	0	0
63	Lit	Nemunas	14	10	0	14	0	0	0	0	0	0	0	0	0	1	1	0	0	1
64	Lit	Nemunas	10	14	0	45	10	0	0	0	0	3	0	0	0	1	0	1	0	2
65	Lit	Neris	6	10	0	11	0	0	0	0	0	3	0	0	0	1	0	1	0	0
66	Lit	Neris	8	11	0	11	0	0	0	0	0	2	0	0	0	1	0	1	0	0
67	Lux	Alzette	100	26	59	31	5	45	57	0	231	10	3	2	1	3	1	12	1	1
68	Lux	Moselle	97	16	13	9	4	0	7	48	72	6	7	1	1	3	1	19	1	0
69	Lux	Sûre	25	9	9	27	0	0	0	0	21	2	0	0	0	1	0	16	0	0
70	Malta	Bahrija Valley	6	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
71	Malta	Wied il-Luq	9	7	0	0	0	0	0	0	0	4	0	0	1	10	1	21	1	0
72	Malta	Wied tal-Lunzjata	14	2	0	0	0	0	0	0	0	0	0	0	0	1	0	1	0	0
73	NL	Meuse	24	23	32	9	10	0	10	16	187	35	0	2	2	7	1	10	1	1
74	NL	Rhine	8	10	3	11	0	0	14	14	0	6	0	4	1	9	1	16	0	0
75	NL	Rhine/Meuse	13	10	1	10	4	0	13	10	0	3	3	3	1	16	1	22	0	0
76	NL	Scheldt	10	0	0	63	7	0	18	0	0	1	0	19	6	73	2	110	1	1
77	No	Glomma	19	19	0	5	0	0	0	0	6	0	0	0	1	1	0	0	0	1
78	No	Alna	30	11	42	0	0	0	0	0	140	0	0	38	3	6	2	21	1	0
79	Po	Vistula	17	8	0	6	0	0	0	0	0	7	0	0	0	2	0	4	0	0
80	Po	Vistula	20	9	6	5	0	0	0	0	0	3	0	0	0	1	0	3	0	0

No.	Country	River	Benzo- triazole	Caffeine	Desethyl- Atrazine	Carbamazepine	Sulfamethox azole	Simazine	Desethylter- butylazine	Methylbenzo triazole	Atrazine	Isoproturon	Diuron	Terbutyl- azine	NPE1C	Nonylphenol	Bisphenol A	Estrone	tert-OP
40	Ge	Rhine	591	250	10	130	37	9	8	326	0	189	10	3	229	0	52	0	0
41	Ge	Rhine	279	118	6	71	15	12	4	218	2	16	14	2	171	0	18	0	16
42	Ge	Saale	358	259	0	218	27	8	23	181	1	50	4	13	180	0	0	0	0
43	Ge	Elbe	355	51	0	215	42	4	11	279	1	25	24	15	202	0	0	0	0
44	Ge	Oder	177	71	6	197	43	0	2	241	3	9	61	2	609	0	0	0	0
45	Ge	Main	811	100	22	258	78	68	18	316	4	129	5	6	295	0	0	0	0
46	Ge	Rhine	272	74	7	89	19	0	4	170	2	0	12	4	161	0	46	0	0
47	Ge	Weser	302	97	4	125	35	0	7	199	1	59	9	3	280	0	0	0	0
48	Ge	Mulde	300	158	0	186	25	19	22	165	1	23	54	27	188	0	18	0	0
49	Ge	Elbe	276	105	4	162	42	0	12	217	2	8	23	7	123	0	10	0	0
50	Ge	Mosel	685	242	7	173	44	5	4	1092	2	74	17	3	570	0	13	0	0
51	Ge	Havel	680	63	0	380	64	0	10	1186	0	4	11	4	351	0	0	0	0
52	Ge	Oder	98	140	3	169	41	0	2	142	2	15	21	3	240	0	0	0	0
53	Ge	Fulda	527	156	5	176	56	0	8	343	1	63	5	4	526	0	0	0	0
54	Greece	Evrotas	0	20	0	0	0	0	0	501	0	0	0	1	89	0	0	0	0
55	Hun	Sio	125	60	45	293	46	0	73	432	30	6	0	41	408	0	0	0	0
56	Hun	Sajo	146	131	11	201	70	0	5	1895	5	6	46	4	1370	0	0	0	0
57	Hun	Raba	128	41	17	164	0	0	18	88	4	6	0	15	472	0	0	0	0
58	Hun	Pecs viz	226	62	18	735	36	0	4	121	4	45	35	8	473	0	0	0	0
59	Hun	Tisza	25	177	0	40	30	0	3	67	4	2	0	2	266	0	11	0	0
60	Hun	Hosszureti Patak	1636	51	0	3192	275	0	13	1132	7	0	5	10	1430	0	0	0	0
61	Ir	Liffey	309	389	0	55	7	0	0	82	0	4	0	0	244	75	0	0	0
62	It	Tevere	238	436	0	77	68	0	3	108	0	0	0	3	350	200	73	11	0
63	Lit	Nemunas	0	8	0	10	6	0	0	0	0	0	0	0	41	0	0	0	0
64	Lit	Nemunas	7	36	0	13	8	0	0	0	0	0	0	0	44	0	0	0	0
65	Lit	Neris	11	32	0	16	16	0	0	0	0	0	0	0	50	0	0	0	0
66	Lit	Neris	15	30	0	17	17	0	0	0	1	0	0	0	30	0	0	0	0
67	Lux	Alzette	806	972	10	69	11	22	61	762	2	264	30	29	353	0	0	0	0
68	Lux	Moselle	317	773	12	60	15	10	5	975	2	165	29	2	468	0	0	0	0
69	Lux	Sûre	125	364	0	17	0	0	13	118	1	17	14	11	77	0	0	0	0
70	Malta	Bahrja Valley	7	4	0	0	0	0	0	0	0	0	0	0	32	0	0	0	0
71	Malta	Wied il-Luq	150	154	0	314	10	0	5	47	0	0	42	11	220	0	15	0	0
72	Malta	Wied tal-Lunzjata	3	9	3	0	0	26	5	0	0	0	1	1	109	0	25	0	0
73	NL	Meuse	601	120	20	112	20	14	6	722	3	10	58	15	266	0	279	4	0
74	NL	Rhine	388	37	11	143	43	0	13	209	2	24	18	7	100	0	47	0	0
75	NL	Rhine/Meuse	332	25	8	123	38	0	8	222	3	17	25	6	33	50	30	0	0
76	NL	Scheldt	471	0	8	203	32	90	40	745	6	22	151	36	185	0	0	0	0
77	No	Glomma	68	0	0	27	0	0	0	136	0	0	0	0	12	0	0	0	0
78	No	Alna	0	33	0	0	0	0	0	0	0	0	0	0	68	0	40	0	0
79	Po	Vistula	224	45	0	172	55	0	0	141	0	1	12	0	179	0	0	0	0
80	Po	Vistula	92	63	0	110	44	0	0	117	1	1	13	0	199	0	0	0	0

No.	Country	River	Nitrophenol	2,4-Dinitrophenol	Naproxen	Bentazone	2,4-D	Ketoprofen	Mecoprop	Bezafibrate	Ibuprofen	Diclofenac	Gemfibrozil	PFHxA	PFHpA	PFOA	PFNA	PFOS	PFDA	PFUnA
81	Po	Vistula	24	12	5	4	0	0	0	0	0	3	0	0	0	1	0	6	0	0
82	Ro	Somez Mic	25	10	0	1	81	0	0	0	0	52	0	0	0	1	0	1	0	0
83	Ro	Somez Mic	446	0	0	1	133	239	0	4	198	209	0	0	1	1	0	4	0	0
84	Ro	Somez Mic	107	34	0	4	53	0	0	4	151	142	0	0	0	1	0	1	0	0
85	Ro	Somez Mare	34	12	0	2	22	14	0	1	61	78	0	0	0	1	0	0	0	0
86	Slovenia	Krka	28	7	1	4	0	8	0	0	0	1	0	0	0	1	0	4	0	0
87	Slovenia	Krka	21	9	10	14	0	29	13	4	77	20	5	109	27	40	3	1371	2	1
88	Slovenia	Krka	7	10	6	20	0	0	0	0	0	5	0	0	0	1	0	3	0	0
89	Slovenia	Sava	6	9	11	5	0	0	0	0	6	2	0	6	0	1	0	5	0	0
90	Slovenia	Ljubljana	23	5	8	13	0	0	0	0	3	1	0	0	0	1	0	3	0	0
91	Slovenia	Ljubljana	11	4	5	5	0	0	0	0	2	0	0	0	0	1	0	2	0	0
92	Slovenia	Drava	29	10	0	2	2	6	0	3	0	1	0	0	0	1	0	2	0	0
93	Slovenia	Drava	30	10	119	2	4	17	0	3	18	2	0	0	0	1	0	2	0	0
94	Spain	Ebro	28	10	7	123	27	0	0	0	0	0	17	0	1	2	0	4	1	1
95	Spain	Llobregat	1619	131	131	0	44	0	74	148	2728	41	731	17	0	43	15	254	1	1
96	Spain	Besos	41	0	25	14	21	0	70	56	0	46	851	11	8	41	13	275	6	1
97	Spain	Sar	127	0	532	0	27	0	0	89	4576	51	464	0	0	6	0	6	1	0
98	Sweden	Dalalven	7	2	0	0	0	0	0	0	0	0	0	0	1	2	1	4	1	1
99	Sweden	Motala	7	7	0	6	0	0	0	0	0	0	0	0	1	1	1	4	0	0
100	Sweden	Norrstrom	8	6	0	2	0	0	0	0	0	0	0	1	1	3	1	12	0	0
101	Sweden	Fyrisan	8	5	0	3	0	0	0	0	0	1	3	2	1	3	1	21	1	1
102	Sweden	Eman	11	0	0	0	0	0	0	0	0	0	0	0	1	2	1	1	0	0
103	Sweden	Viskan	13	6	0	2	0	32	0	0	0	0	0	0	1	2	1	3	0	0
104	Sweden	Gota Alv	10	0	7	0	0	0	0	0	5	1	7	0	1	3	1	4	0	1
105	Swiss	Murg	33	9	12	0	0	0	14	0	0	23	0	3	2	8	3	135	1	1
106	Swiss	Glatt	16	8	11	4	0	0	53	16	0	28	2	3	2	9	1	42	1	1
107	Swiss	Birs	9	0	5	0	0	0	0	9	11	5	0	2	1	3	0	28	0	0
108	Swiss	Thur	18	8	4	2	0	0	22	0	0	8	0	0	1	3	1	59	0	0
109	Swiss	Aare	10	0	6	3	0	0	12	6	4	4	0	0	1	3	1	15	0	0
110	Swiss	Reuss	6	6	3	0	0	0	8	0	0	3	0	0	0	2	1	13	0	0
111	Swiss	Limmat	0	10	7	0	4	0	14	4	5	8	0	0	1	2	1	15	1	0
112	UK	Wyre	14	13	0	0	14	0	0	0	0	0	0	7	2	100	1	2	1	1
113	UK	Lune	37	50	3	0	38	0	7	6	9	0	0	12	1	1	1	7	0	0
114	UK	Clyde	43	24	83	0	26	0	22	45	500	10	0	0	1	3	1	6	0	0
115	UK	Humber	11	10	0	14	21	0	61	24	0	0	0	26	3	75	3	33	1	0
116	UK	Tees	14	18	30	0	9	0	13	34	35	3	0	0	1	5	1	5	0	0
117	UK	Mersey	16	23	2	0	57	0	106	62	16	10	0	2	2	25	1	22	1	0
118	UK	Forth	8	0	0	0	0	0	0	0	4	0	0	0	0	1	0	2	0	0
119	UK	Severn	19	23	12	19	35	0	33	36	62	6	0	4	2	7	1	238	1	0
120	UK	Ouse	18	5	18	4	3	0	10	28	56	5	2	0	1	1	1	7	0	0
121	Tu	Sakarya	62	26	47	0	34	0	0	0	27	0	20	0	1	4	1	4	0	0
122	Tu	Dilderesi	3471	0	2027	127	1221	0	0	0	31323	43	31	0	0	15	1	529	0	0

No.	Country	River	Benzo- triazole	Caffeine	Desethyl- Atrazine	Carbamazepine	Sulfamethox azole	Simazine	Desethyl- butylazine	Methylbenzo triazole	Atrazine	Isoproturon	Diuron	Terbutyl- azine	NPE1C	Nonylphenol	Bisphenol A	Estrone	tert-OP
81	Po	Vistula	82	85	0	105	44	0	1	91	1	1	14	0	197	0	14	0	0
82	Ro	Somez Mic	0	4	3	0	0	0	0	89	17	0	0	1	0	0	0	0	0
83	Ro	Somez Mic	99	195	0	112	11	0	9	320	7	8	13	2	107	440	112	14	0
84	Ro	Somez Mic	33	156	6	45	19	0	8	165	6	3	2	6	75	50	0	13	0
85	Ro	Somez Mare	17	76	4	13	7	49	2	136	46	0	0	1	11	60	13	3	0
86	Slovenia	Krka	20	23	6	6	4	0	3	0	1	3	0	2	11	0	32	0	0
87	Slovenia	Krka	48	50	0	10	6	0	18	104	2	2	0	10	26	0	121	0	0
88	Slovenia	Krka	39	1735	0	7	8	0	0	32	2	3	0	0	184	0	0	0	0
89	Slovenia	Sava	232	0	0	14	13	0	0	59	1	1	0	0	149	250	0	0	0
90	Slovenia	Ljubljana	70	91	6	14	3	0	4	13	1	1	0	3	32	0	32	0	0
91	Slovenia	Ljubljana	32	94	0	7	3	0	9	0	0	1	0	5	14	0	63	0	0
92	Slovenia	Drava	51	123	0	16	0	0	0	22	0	2	0	1	40	0	0	0	0
93	Slovenia	Drava	293	323	0	15	0	0	0	21	1	2	1	1	25	0	21	0	0
94	Spain	Ebro	85	66	80	10	11	35	76	80	10	3	14	41	864	0	0	0	0
95	Spain	Llobregat	2373	4108	0	128	219	55	39	2891	1	0	278	78	654	305	82	6	191
96	Spain	Besos	2269	1547	0	219	144	61	37	2769	8	12	277	86	1194	548	123	0	82
97	Spain	Sar	2309	11296	0	157	416	0	6	1211	0	0	167	4	988	158	0	70	0
98	Sweden	Dalalven	3	15	0	4	0	0	0	38	0	0	0	0	601	0	0	0	0
99	Sweden	Motala	9	9	0	8	0	0	4	0	0	1	0	1	382	0	0	0	0
100	Sweden	Norrstrom	35	59	0	14	0	0	3	32	0	0	17	1	491	0	0	0	0
101	Sweden	Fyrisan	32	11	0	34	0	0	3	0	0	0	2	0	970	0	0	0	0
102	Sweden	Eman	4	5	0	10	0	0	3	0	0	0	0	0	365	0	0	0	0
103	Sweden	Viskan	6	14	0	6	0	0	0	0	0	1	0	0	340	0	17	0	0
104	Sweden	Gota Alv	48	40	0	30	4	0	0	0	0	0	0	0	144	0	0	0	0
105	Swiss	Murg	2032	34	27	239	38	15	8	402	5	26	14	4	276	0	0	0	0
106	Swiss	Glatt	2606	66	35	226	80	20	13	464	7	29	16	8	203	0	0	0	0
107	Swiss	Birs	490	58	17	61	22	0	3	140	3	5	0	0	98	0	0	0	0
108	Swiss	Thur	626	23	15	119	39	17	4	187	4	87	60	2	514	123	39	0	0
109	Swiss	Aare	315	41	17	39	12	0	9	140	0	10	0	2	221	0	8	0	0
110	Swiss	Reuss	289	0	6	28	11	0	5	117	2	3	0	0	463	0	0	0	0
111	Swiss	Limmat	486	44	6	55	37	9	5	164	1	2	19	2	507	0	0	0	0
112	UK	Wyre	63	0	0	2	0	0	0	0	2	0	7	0	0	320	0	0	0
113	UK	Lune	39	0	0	5	0	0	0	0	0	0	2	0	163	0	0	0	0
114	UK	Clyde	359	40	12	92	4	0	14	0	1	22	30	0	91	200	43	4	0
115	UK	Humber	323	154	12	121	5	0	4	200	1	30	41	0	64	230	0	0	0
116	UK	Tees	196	67	0	89	5	0	0	60	1	5	2	0	40	0	0	0	0
117	UK	Mersey	535	28	0	154	7	0	3	380	1	77	864	80	64	230	0	0	0
118	UK	Forth	24	8	0	6	0	0	0	0	0	1	7	0	0	0	0	0	0
119	UK	Severn	1088	81	6	205	10	23	1	382	2	4	20	1	158	0	0	0	0
120	UK	Ouse	517	230	0	122	6	28	0	91	0	39	7	0	273	0	0	3	0
121	Tu	Sakarya	301	55	0	68	42	0	0	107	0	0	0	0	1465	280	59	30	300
122	Tu	Dilderesi	7997	39813	0	306	387	0	0	19396	0	18	115	0	976	500	300	0	557

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Abstract

This study provides the first EU-wide reconnaissance of the occurrence of polar organic persistent pollutants in European river waters. 122 individual water samples from over 100 European rivers, streams or similar water bodies from 27 European Countries were analysed for 35 selected compounds, comprising pharmaceuticals (e.g. carbamazepine, diclofenac), antibiotics (sulfamethoxazole), pesticides (e.g. 2,4-D, mecoprop, bentazone, terbutylazine), perfluorinated compounds PFCs (PFOS, PFOA), benzotriazoles (corrosion inhibitors), hormones (estrone, estradiol), and alkylphenolics (bisphenol A, nonylphenol). Only the dissolved (liquid) water phase, and not the suspended material was investigated.

Around 40 laboratories actively participated in this sampling and monitoring exercise organised by the Joint Research Centre's Institute for Environment and Sustainability (JRC-IES) of the European Commission (EC) in autumn 2007. The selection of sampling sites was done by the participating EU Member States.

The most frequently and at the highest concentration levels detected compounds were benzotriazole, caffeine, carbamazepine, tolyltriazole, and nonylphenoxy acetic acid (NPE₁C). Other important substances identified were naproxen, bezafibrate, ibuprofen, gemfibrozil, PFOS, PFOA, sulfamethoxazole, isoproturon, diuron, and nonylphenol. The highest median concentrations of all samples were measured for benzotriazole (226 ng/L), caffeine (72 ng/L), carbamazepine (75 ng/L), tolyltriazole (140 ng/L), and NPE₁C (233 ng/L).

Relatively high perfluorooctanoate (PFOA) levels were detected in the Rivers Danube, Scheldt, Rhone, and Wyre, and "elevated" perfluorooctanesulfonate (PFOS) concentrations in the Rivers Scheldt, Seine, Krka, Severn, Rhine, and Llobregat. A higher median concentration for all river samples was found for PFOS (6 ng/L), compared to PFOA (3 ng/L).

Only about 10 % of the river water samples analysed could be classified as "very clean" in terms of chemical pollution, since they contained only a few compounds in very low concentrations. The most pristine water samples came from Estonia, Lithuania, and Sweden.

For the target compounds chosen, we are proposing limit values in surface waters which are not based on eco-toxicological considerations; these warning levels are (for most compounds) close to the 90th percentile of all water samples analysed.

A first EU-wide data set has been created on the occurrence of polar persistent pollutants in river surface waters to be used for continental scale risk assessment and related decision support.

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